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A JOURNAL OF EXPERIMENTAL AND THEORETICAL PHYSICS

CONDUCTED
WITH THE CO-OPERATION OF THE

AMERICAN PHYSICAL SOCIETY

BY

EDWARD L. NICHOLS
ERNEST MERRITT, and FREDERICK BEDELL

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OCTOBER, 1909

Application of Gibbs-Helmholtz Equation to Concentration Cells. FRANK J. MELLENCAMP 329

Anode Drop with Hot CaO Cathode. C. D. CHILD 351

The Residual of Inductance and Capacity in Resistance Coils. A Standard Resistance with Balanced Inductance and Capacity. S. LEROY BROWN 369

A Study of the Reflecting Power of Metals as Dependent on the Refractive Index of the Surrounding Medium. L. R. INGERSOLL and R. T. BIRGE 392

On the Photo-electric Effect with the Alkali Metals. II. F. K. RICHTMYER 404

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THE

PHYSICAL REVIEW.

APPLICATION OF GIBBS-HELMHOLTZ EQUATION TO CONCENTRATION CELLS.

By Frank J. Mellencamp.

Introduction.

UP to the present time there is no theory that satisfactorily accounts for the E.M.F. of concentration cells. The Nernst equation, which is based upon the gas law, applies only to very dilute solutions — millinormal and under. For somewhat greater concentrations it has to be modified, and for strong solutions it no longer holds. It has been pointed out [1] that the Gibbs-Helmholtz equation applies when the heats of reaction and dilution are so small that they may be neglected. This also restricts the solutions to very dilute ones. The present research has for its object, in general, the application of the Gibbs-Helmholtz equation to concentration cells, and in particular, to cells in which the heat of dilution is not negligible, and to show how to take this factor into account. The class of cells to which application is made is that in which the two electrodes are composed of amalgams of the same metal immersed in a salt solution of the metal, the concentration of the amalgams being the same, but that of the solution being different at the two electrodes.

Historical.

Robert Mayer [2] was one of the first to point out that there existed a relation between the change in chemical energy and the electrical

[1] Trans. Am. Electrochem. Soc., 1, 32, 1906.

[2] Mayer, Die Organische Bewegung in ihrem Zusammenhange mit dem Stoffwechsel.

energy of the current. Helmholtz[1] was of the opinion that all the chemical energy lost reappeared in the electrical form. This opinion was also held by Sir William Thomson,[2] J. Bosscha[3] and others. Later investigations by Raoult,[4] Thomsen[5] and Braun[6] showed experimentally that the electrical energy may be either greater or less than the heat of chemical reaction. Gibbs[7] and Helmholtz[8] theoretically came to the same conclusion. Helmholtz finally put this theory into the form in which it is usually found. He called that portion of the whole heat energy which can be transformed into electrical energy, "free energy," that portion which cannot be transformed, "bound energy" and the sum of these two "total energy." The theory stated in this form is known as the Gibbs-Helmholtz equation.

Numerous examples[9] of the Gibbs-Helmholtz equation have been worked out for voltaic cells, but no general application has been made to concentration cells. Richard and Lewis[10] applied the equation to concentration cells for determining the heats of amalgamation from the temperature coefficient when amalgam was used for one of the electrodes and pure metal for the other.

Carhart,[11] in his thermoelectric theory of concentration cells, maintains that concentration cells are devices for converting heat of their surroundings into electrical energy, and that whenever the heat of reaction and dilution is negligible, the last term only of the Gibbs-Helmholtz equation, $T \cdot dE/dT$, remains and represents the E.M.F.

[1] Ostwald, Klassiker der exakten Wissenschaften, Nr. 1.

[2] Phil. Mag., 2, 429, 1851; 2, 551, 1851.

[3] Pog. Ann. Phys., 101–517, 1857; 103, 1858; 105, 396, 1858.

[4] Ann. de Chimie et de Phys., 4, 392, 1856.

[5] Wied. Ann. Phys., 11, 246, 1880.

[6] Wied. Ann. Phys., 5, 183, 1878; 16, 561, 1882; 17, 593, 1882.

[7] Trans. of Connecticut Acad., 3, 588, 1878.

[8] Berl. Sitsungs., 22, 1884.

[9] Czapski, Wied. Ann. Phys., 21, 209, 1884. Gockel, Wied. Ann. Phys., 24, 618, 1885. Jahn, Wied. Ann. Phys., 28, 21, 1886; 28, 491, 1886; 28, 498, 1886. Nernst & Bugarsky, Zeit. f. anorg. Chem., 14, 145, 1890. Poincaré, Ann. de Chimie et de Phys., 21, 344, 1890. Oswald & Miller, Zeit. Phys. Chem., 34, 62, 1900; 34, 612, 1900. Cohen, Zeit. Phys. Chem., 60, 707, 1901. Lorenz, Electrolysis of Fused Salts, Vol. 3. Lorenz, Zeit. Phys. Chem., 63, 121, 1908.

[10] Am. Acad. of Arts and Sciences, 34, 87, 1898.

[11] Trans. Am. Electrochem. Soc., 2, 123, 1902.

of the cell. Application[1] was made to two cells of the type, Ag — $AgNo_3$ conc. — $AgNo_3$ dil. — Ag, and Cd.Hg — $n/10$ $CdSO_4$ — $n/100$ $CdSO_4$ — Cd.Hg. The agreement between the calculated values and the observed values was very good but in both cases the calculated values were low because the heat of dilution was not taken into account.

In 1907 Richards and Forbes[2] reported work done on concentration cells in which the difference of concentration was in the amalgams comprising the electrodes. Heats of dilution of cadmium and zinc amalgams were measured with a specially devised calorimeter. The heat of dilution of a 3 per cent. cadmium amalgam was so small as to be negligible. In this case the last term of the Gibbs-Helmholtz equation was found to represent the E.M.F. of the cell. For the zinc amalgam, the heat of dilution is not negligible. No application of the Gibbs-Helmholtz equation was made to such cells.

For the last two decades numerous examples of concentration cells have been worked out for the purpose of verifying the equations of Nernst and Planck, but as far as is known to the writer the Gibbs-Helmholtz equation has not been applied to concentration cells of any type so as to take into account the heat of dilution.

Theoretical.

According to the Gibbs-Helmholtz equation wich is based upon fundamental principles of thermodynamics,

$$E = \frac{H}{nF} + T\frac{dE}{dT}, \qquad (1)$$

in which E represents the E.M.F. of the cell; H the heat of reaction; n the valence of the ion; F the number of coulombs transported by a gram equivalent of the ion; T the absolute temperature.

Equation (1) when written

$$nFE = H + nFT\frac{dE}{dT} \qquad (2)$$

gives the conditions under which the electr ca energy nFE, is a

[1] Trans. Am. Electrochem. Soc., 1, 32, 1906.
[2] Zeit. Phys. Chem., 58, 683, 1907.

measure of the heat of reaction of a cell. It is to be observed that $nFE = H$ whenever $dE/dT = 0$, or $T = 0$. In other words, the electrical energy of a cell is equal to the heat of reaction, (1) when the temperature coefficient is zero, (2) when the absolute temperature is zero. If $dE/dT > 0$, or the temperature coefficient is positive, the electrical energy is greater than the heat of reaction. If $dE/dT < 0$, or the temperature coefficient negative, the electrical energy is less that the heat of reaction. In the former case the cell absorbs heat from the surroundings; in the latter, it evolves heat. The total electrical energy of the cell may be calculated by determining the heat of reaction and the temperature coefficient.

If equation (2) is written

$$H = nF\left(E - T\frac{dE}{dT}\right) \qquad (3)$$

an expression is obtained by means of which the heat of reaction may be calculated by merely measuring the E.M.F. at different temperatures. It is to be noted in this case that $H = 0$ whenever $E = T \cdot dE/dT$, or the heat of reaction is equal to zero whenever the E.M.F. of the cells equals $T \cdot dE/dT$ as is approximately the case for concentration cells with dilute solutions; $H > 0$ whenever $E > T \cdot dE/dT$, or the heat of reaction is positive whenever the E.M.F. of the cell is greater than $T \cdot dE/dT$; $H < 0$ whenever $E < T \cdot dE/dT$, or the heat of reaction is negative whenever the E.M.F. is less than $T \cdot dE/dT$.

These equations were applied to cells of the following general type: Amalgam — concentrated salt solution of metal in amalgam — dilute salt solution of metal in amalgam — amalgam. In all cases the amalgam used for the two electrodes was of the same kind and concentration; the solutions in the two legs of the cell were of the same salt but of different concentration. Only those solutions were used for which the heats of dilution were known.

For cells of the above type the heat of dilution becomes the heat of reaction. If we dilute from any initial concentration to the concentrations of the solutions in the two legs of the cell, the heats of dilution, in general, are different. This difference is available as energy to produce E.M.F. represented by the first term of the

Gibbs-Helmholtz equation. The electrode in the more dilute solution is the anode, that is, the electrode by which the current enters the cell. Whenever the heat of dilution is positive, that is, when dilution generates heat, then more heat is generated for the entrance of a gram-equivalent of the electrode at the anode than is absorbed by the removal of an equal amount at the cathode. If the heat of dilution is negative, that is, if dilution absorbs heat, then more heat is absorbed at the anode than is generated at the cathode. Let us suppose the quantities of the two solutions so great that the entrance of a gram-equivalent at the anode and the removal of an equal amount from the solution about the cathode do not change the concentration of the solutions. Now when the gram-equivalent of metal at the anode goes into solution it becomes a salt and is diluted down to the same concentration as that of the solution surrounding the anode; at the same time an equal amount of the metal is removed from the more concentrated solution surrounding the cathode. When the heat of dilution is positive, this latter operation absorbs less energy than is derived from the former; when negative the former absorbs more energy than is generated by the latter. This difference of energy is available to produce E.M.F. When it is positive the E.M.F. is directed within the cell from the more dilute to the concentrated solution; when negative, from the concentrated to the more dilute.

Description of Apparatus.

For the accurate determination of the E.M.F. of concentration cells in which the electrolytes on the two sides of the cell are of different concentration two things are especially desired in the construction of the apparatus. First, that the temperature of the two legs of the cell be kept the same and remain constant for any desired length of time; and second, that during this time there shall be no mixing of the electrolytes. To satisfy the first condition, three thermostats were employed, one for the warm bath, the second for the intermediate, and a third for the cold. The temperature in these could be maintained constant to within 0.02° C. by means of a toluene-mercury regulator. Beckmann thermometers were employed for reading the temperatures. The E.M.F. was measured

by means of an Otto Wolff potentiometer which reads directly to 0.00001 volt. A Weston normal cell was used as a standard of comparison.

The concentration cell was set up as shown in Fig. 1. A_1 and A_2 represent the two legs of the cell, which are connected by means of a bent tube containing a filter paper plug *h* and provided with a glass stop-cock *S*; *a*, *a*, the two electrodes; *b*, *b*, the two electrolytes. The electrodes *a*, *a* are composed of glass cups *c*, *c* about 2 cm. in diameter, into which are fused glass tubes. Through the

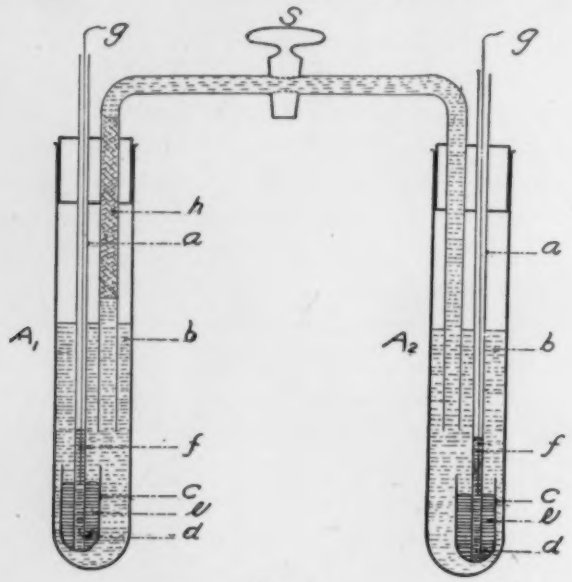

Fig. 1.

tubes near the bottom are sealed short platinum wires *d*, *d*, which make connection with the amalgams *e*, *e* in the cups and the mercury *f*, *f* inside the tubes. Copper wires *g*, *g* lead from the mercury in the tube direct to the potentiometer.

The filter paper plug *h* in the arm of the tube making connection with the two solutions deserves special attention, as it is this that prevents the mixing of the electrolytes, and thus meets the requirements of the second condition. The solutions in the two legs of the cell were maintained at the same level and the stop-cock kept open only while readings were being taken. The cell was suitably

supported in the thermostat so that the temperature remained the same for both legs. The filter paper plug was near the end of the tube so that the junction of the liquids might be maintained at the same temperature as the electrodes.

Preparation of Materials.

Solutions.

Zinc and cadmium sulphates were prepared in practically the same manner. The chemically pure salt was dissolved in twice distilled water to form a saturated solution, which was allowed to evaporate until about three fourths of the salt had crystallized out. The crystals were washed several times with distilled water and then, before drying, transferred to a closed vessel where they were kept until ready for use. It is essential that the salt be dry but at the same time lose none of its water of crystallization; so a portion was carefully dried each time just before making up the solutions. The solutions were prepared as follows: $ZnSO_4 \cdot 50H_2O$, means that for every gram-molecule of anhydrous salt 50 gram-molecules of water, or 900.76 grams of water are required. One gram-molecule of $ZnSO_4 \cdot 7H_2O$ weighs 287.67 grams; of this 161.46 grams are anhydrous salt, and 126.11 grams water of crystallization. If hydrated salt be used, then 126.11 grams must be subtracted from 900.76 grams, thus leaving 774.65 grams of water to be added to the gram-molecule of the hydrated salt.

The lead nitrate was recrystallized from the pure salt, dried on a watch glass and kept in a desiccator until ready for use. The solutions were prepared by weight similar to the sulphate.

The preparation of the zinc chloride solutions will be described in connection with the zinc chloride cell.

Amalgams.

The mercury used for the amalgams was prepared by double distillation. For most of the work the amalgams were prepared, electrolytically from an acid solution of the purified salts; however, the observations showed no difference between these and others prepared by the fusion of the metal and mercury. Since the exact concentration of the amalgams is not essential, they were

kept under an acid solution until ready for use, and then, just before using, thoroughly washed with distilled water.

EXPERIMENTS AND RESULTS.

Zinc Sulphate Cells.

Amalgam electrodes are best adapted for work on electrode potential. Since with pure metals it is very difficult to prevent oxidation or exclude occluded gases, variable and unsatisfactory results must necessarily follow. To obtain consistent results the electrodes must remain reasonably constant for days. Amalgams best fulfill these conditions. Preliminary tests were made to see what amalgams were best adapted for zinc sulphate cells. A series of amalgams ranging from .1 to 15 per cent. were used for this purpose. The amalgams must not change phase in the temperature interval employed, that is, they must remain either solid or liquid throughout the test. Change of phase causes a break in the temperature coefficient. Amalgams below one per cent. and above 10 per cent. fulfill these conditions, the former remaining liquid throughout; the latter, solid. Amalgams of a little less than one per cent. were finally chosen as best adapted to the following work because an amalgam which is much more dilute oxidizes readily, and the solid is less convenient to handle. The solutions used were prepared from the freshly dried $ZnSO_4 \cdot 7H_2O$ as described. High temperature could not be employed because zinc sulphate at 39° changes from the heptahydrate to the hexahydrate salt, and irregularities in readings occurred when this temperature was approached. These irregularities were probably due to the surface condition of the amalgam changing with the least possible current.

The cell was set up in the following manner: All parts were washed with nitric acid, then treated with cleansing solution, after which they were thoroughly rinsed with distilled water and carefully dried. The two legs of the cells were filled about two thirds full with their respective electrolytes. Into one end of the connecting tube was packed chemically pure filter paper, as shown in Fig. 1. The tube was then filled with the two electrolytes, the denser solution in the shorter arm and the more dilute in the longer arm, the two meeting at about the middle of the filter paper plug.

The amalgam, which had previously been prepared and kept under a dilute solution of sulphuric acid, was washed with distilled water and then transferred to the small cups by means of a clean pipette. The electrodes were at once put into the solutions of the two legs, leaving them exposed to the air but a few seconds; the connecting tube was put in place and the legs of the cell closed with rubber stoppers, which had been soaked in distilled water for several days. When all had been adjusted as shown in Fig. 1, the stoppers were covered with paraffin.

The following combination was first used:

$$Zn \cdot Hg - ZnSO_4 \cdot 50H_2O - ZnSO_4 \cdot 400H_2O - Zn \cdot Hg.$$

Before recording observations, the cell was allowed to stand a few hours, until equilibrium had been reached. In general it took a few hours before the readings of the cells became constant. There was no regularity in the shifting of the preliminary readings; some cells assumed a high initial value and gradually fell to constancy, others started with a low initial value and rose, while still others remained constant from the very first.

TABLE I.

Date.	Temp.	E.M.F.
August 30, 8:00 P. M.	0	0.01581
" " 8:30 "	0	0.01580
" " 8:40 "	0	0.01580
" 31, 9:00 A. M.	25	0.01708
" " 9:15 "	25	0.01708
" " 10:00 "	0	0.01578
" " 10:30 "	0	0.01578
" " 11:00 "	25	0.01711
" " 1:45 "	25	0.01712
" " 3:30 "	25	0.01713
" " 3:55 "	0	0.01580
" " 4:05 "	0	0.01577
" " 4:30 "	0	0.01578
" " 7:00 "	0	0.01579
" " 7:30 "	25	0.01708
" " 8:00 "	25	0.01710

Table I. gives the readings of cell 1*b* for a period of twenty-four hours after beginning to record observations. This is a fair sample of the constancy of the cells used. The readings show that the changes due to oxidation or other causes are so small as not to

materially affect the results. The readings also show that the cell practically assumes the same value when brought back to the same temperature, otherwise it was discarded as in all subsequent work. Irregularities in nearly all cases were traced to some defect in the construction of the cells, such as a crack in the glass where the platinum was sealed through, or to change of phase for some of the materials. In fact, it seems that irregularities due to change of phase became evident several degrees before the temperature was reached at which this change nominally takes place. In most cases the temperature coefficient used was the mean of three different sets of readings as shown in Table I.

Table II. gives the results of the investigation of zinc sulphate cells. E_h is the E.M.F. due to the heat of dilution and $T \cdot dE/dT$ is the E.M.F. derived from the heat of the surroundings. All cells were set up and manipulated in the general manner just described. The solutions used were those for which the heats of dilution had been determined by Thomsen.[1] The most concentrated solution used was that of $ZnSO_4 \cdot 50H_2O$. $ZnSO_4 20H_2O$ was tried in the preliminary work, but the salt began to crystallize out before the lower temperature was reached, thus restricting the range for determining the temperature coefficient to higher readings. This fact made it undesirable as an electrolyte; consequently this solution was rejected. For the remaining solutions all possible combinations were made.

Two sets of comparisons are given in the table — one consisting of two columns of E.M.F.'s and the other consisting of two columns of heats of dilution. The computed E.M.F. for the first set is obtained in the following manner. According to Thomsen, for one gram-molecule of $ZnSO_4 \cdot 20H_2O$ diluted to $ZnSO_4 \cdot 50H_2O$, 318 calories of heat are generated. Also, $ZnSO_4 \cdot 20H_2O$ diluted to $ZnSO_4 \cdot 400H_2O$ generates 400 calories. Hence one gram-molecule of $ZnSO_4 \cdot 50H_2O$ diluted to $ZnSO_4 \cdot 400H_2O$ generates 82 calories. Since this heat of dilution is positive, it is free energy and gives rise to

$$\frac{82 \times 4.189}{2 \times 96{,}500} = 0.00178 \text{ volt E.M.F.}$$

[1] Thermochem. Untersuchungen, J. Thomsen (see Table X.).

TABLE II.

Solutions.	Cells.	dE/dT	$T \cdot dE/dT$ at 25°.	E_h	Comp. E.M.F.	Obs. E.M.F.	Comp. Heat of Dil. in Cal.	Obs. Heat of Dil. in Cal.
$ZnSO_4 \cdot 50H_2O$	1*a*	0.0000528	0.01573	0.00178	0.01751	0.01713	65	82
	1*b*	0.0000524	0.01561	"	0.01739	0.01710	69	"
$ZnSO_4 \cdot 400H_2O$	1*c*	0.0000510	0.01520	"	0.01698	0.01701	83	"
	1*d*	0.0000510	0.01520	"	0.01698	0.01711	88	"
	1	0.0000518	0.01544	0.00178	0.01722	0.01709	76	82
$ZnSO_4 \cdot 50H_2O$	2*a*	0.0000352	0.01029	0.00125	0.01193	0.01162	53	67
$ZnSO_4 \cdot 200H_2O$	2*b*	0.0000344	0.01045	"	0.01170	0.01159	62	"
	2*c*	0.0000340	0.01013	"	0.01158	0.01139	58	"
	2	0.0000345	0.01029	0.00125	0.01174	0.01153	57	67
$ZnSO_4 \cdot 100H_2O$	3*a*	0.0000340	0.01013	0.00072	0.01085	0.01090	35	33
	3*b*	0.0000344	0.01025	"	0.01097	0.01090	30	"
$ZnSO_4 \cdot 400H_2O$	3*c*	0.0000344	0.01025	"	0.01097	0.01081	26	"
	3	0.0000343	0.01021	0.00072	0.01093	0.01087	30	33
$ZnSO_4 \cdot 50H_2O$	4*a*	0.0000174	0.00518	0.00106	0.00624	0.00628	51	49
$ZnSO_4 \cdot 100H_2O$	4*b*	0.0000160	0.00477	"	0.00583	0.00607	60	"
	4	0.0000167	0.00498	0.00106	0.00604	0.00618	56	49
$ZnSO_4 \cdot 100H_2O$	5*a*	0.0000172	0.00512	0.00039	0.00551	0.00541	13	18
$ZnSO_4 \cdot 200H_2O$	5*b*	0.0000180	0.00536	"	0.00575	0.00552	7	"
	5	0.0000176	0.00524	0.00039	0.00563	0.00547	10	18
$ZnSO_4 \cdot 200H_2O$	6*a*	0.0000164	0.00489	0.00033	0.00522	0.00543	25	15
$ZnSO_4 \cdot 400H_2O$	6*b*	0.0000180	0.00536	"	0.00569	0.00556	9	"
	6	0.0000172	0.00513	0.00033	0.00546	0.00550	17	15
2+6	7	0.0000519	0.01542	0.00178	0.01720	0.01703	74	82
4+3	8	0.0000510	0.01519	0.00178	0.01697	0.01708	86	82
4+5+6	9	0.0000515	0.01535	0.00178	0.01713	0.01715	83	82
Mean of 1, 7, 8, 9	10	0.0000515	0.01535	0.00178	0.01713	0.01709	80	82

The temperature coefficient of (10) is 0.0000515, as a mean of the four independent determinations. Hence $T \cdot dE/dT$ at 25° is 298 × 0.0000515 equal to 0.01535. Then E computed equals 0.00178 + 0.01535 = 0.01713 volt, as compared with 0.01709 volt, the observed value at 25°.

To obtain the computed heat of dilution of the second set of comparisons, the process is reversed. The observed E.M.F. at 25°

equals 0.01709 volt, and $T \cdot dE/dT$ equals 0.01535 volt as before. Then 0.01709 — 0.01535 equals 0.00174 volt as the difference of the observed E.M.F. and that due to the heat from the surroundings. This surplus energy arises from the heat of dilution and is equivalent to 80 calories, as compared with 82 calories, observed by Thomsen.

By applying the principle of a cyclic system we obtain three checks on cell 1; the sum of 2 and 6 should equal 1; 3 and 4, equal 1; 4, 5 and 6, equal 1. Thus we obtain independently, four values for the combination $Zn \cdot Hg - ZnSO_4 \cdot 50H_2O - ZnSO_4 \cdot 400H_2O - Zn \cdot Hg$; (10) gives the mean of these four. From a comparison of these four it will be seen that the agreement is very satisfactory. If we compare the computed and observed E.M.F.'s the maximum difference is about one per cent., while for the mean it is less than one fourth of one per cent. Since the heats of dilution account for only about ten per cent. of the total E.M.F., the second set of comparisons is not so favorable from a percentage basis. Comparison of results on a percentage basis does not signify much unless we take into account all the factors which enter the quantities compared. To illustrate: one per cent. difference, between the computed and observed E.M.F. in cell 1, is equivalent to ten per cent. difference between the computed and observed heats of dilution; in cell 6 one per cent. difference in E.M.F. is equivalent to seventeen per cent. difference in heats of dilution.

For ten of the sixteen cells recorded in Table II. the calculated E.M.F. exceeds the observed; the mean difference, as shown above, is less than one fourth of one per cent. With the exception of *2c*, *4a* and *4b* the observed E.M.F. differs from the mean value by less than one per cent. The difference between the observed E.M.F. and that due to $T \cdot dE/dT$ is from five to eighteen per cent. of the whole E.M.F. of the cell and bears no direct relation to either, but is proportional to the heat of dilution as observed calorimetrically. The Gibbs-Helmholtz equation applies rigorously in this case, the deviation being less than the probable experimental error.

Cadmium Sulphate Cells.

For zinc sulphate cells the heat of dilution is relatively small, accounting for only a small portion of the total E.M.F. of the cell, the remainder being due to $T \cdot dE/dT$, the heat absorbed from the surroundings. Extending the investigation to solutions of cadmium sulphate we obtain a cell in which the heat of dilution is relatively large. The study of this cell was taken up in the general manner just described. The amalgam, however, proved more troublesome. With dilute amalgams, the E.M.F. did not consistently return to the same value when brought back to the same temperature. Evidently some change had taken place either in the amalgam or the electrolyte. Since there is no transition point in cadmium sulphate below 74° these irregularities cannot be ascribed to the salt. They might be due to oxidation, as the electrode in the more dilute solution gradually lost its brilliancy and became covered with a thin film. A "time test" made for a period of eighteen days, as given in Table III., shows that the cell remained remarkably constant. After reaching equilibrium, the maximum change in E.M.F. was only 0.00003 volt. Next, cells were set up from which the air had been thoroughly removed, and then saturated with hydrogen. These remained constant at 25° as before, but showed the same irregularities with change of temperature. Thus it seemed altogether unlikely that oxidation was the disturbing factor. Richards and Forbes[1] found that oxidation became evident only with very dilute amalgams.

The potential difference between cadmium amalgam and cad-

TABLE III.

Cell set up November 30, 1908.	25°	0.00532
December 1, 10:00 A. M.	"	0.00520
" 2, 9:00 "	"	0.00526
" 2, 1:20 P. M.	"	0.00525
" 3, 2:00 "	"	0.00527
" 5, 9:00 A. M.	"	0.00524
" 5, 4:00 P. M.	"	0.00526
" 6, 2:00 "	"	0.00527
" 9, 9:00 A. M.	"	0.00527
" 10,	"	0.00526
" 17,	"	0.00525

[1] Zeit. Phys. Chem., 58, 683, 1907.

mium sulphate does not change for amalgams between five and fifteen per cent. Amalgams lying within this interval would therefore seem most favorable; hence six per cent. amalgam was chosen. This amalgam has the further advantage of being a liquid at ordinary temperature. Cells set up with it gave readings which were more constant, consequently more trustworthy. The temperature interval for determining the temperature coefficient was taken from 25° to 40°; at lower temperatures the solid phase appears.

TABLE IV.

Solutions.	Cells.	dE/dT	$T \cdot dE/dT$ at 25°.	E_{25}	Comp. E.M.F.	Obs. E.M.F.	Comp. Heat of Dil. in Cal.	Obs. Heat of Dil. in Cal.
$CdSO_4 \cdot 30 \cdot 6H_2O$	1*a*	0.0000235	0.00700	0.01565	0.02265	0.02205	694	722
$CdSO_4 \cdot 400H_2O$	1*b*	0.0000244	0.00727	"	0.02292	0.02213	685	"
	1*c*	0.0000210	0.00626	"	0.02191	0.02213	732	"
	1	0.0000230	0.00684	0.01565	0.02249	0.02210	704	722
$CdSO_4 \cdot 30 \cdot 6H_2O$	2*a*	0.0000080	0.00238	0.00960	0.01199	0.01176	432	443
$CdSO_4 \cdot 100H_2O$	2*b*	0.0000078	0.00231	"	0.01191	0.01170	434	"
	2	0.0000079	0.00235	0.00960	0.01195	0.01173	433	443
$CdSO_4 \cdot 100H_2O$	3*a*	0.0000155	0.00462	0.00604	0.01066	0.01025	260	279
$CdSO_4 \cdot 400H_2O$	3*b*	0.0000156	0.00465	"	0.01069	0.01038	265	"
	3*c*	0.0000160	0.00477	"	0.01081	0.01052	266	"
	3	0.0000157	0.00468	0.00604	0.01072	0.01038	264	279
$CdSO_4 \cdot 50H_2O$	4*a*	0.0000192	0.00572	0.01082	0.01654	0.01638	492	499
$CdSO_4 \cdot 400H_2O$	4*b*	0.0000200	0.00596	"	0.01678	0.01637	481	"
	4*c*	0.0000185	0.00551	"	0.01633	0.01615	491	"
	4	0.0000192	0.00573	0.01082	0.01655	0.01629	488	499
$CdSO_4 \cdot 50H_2O$								
$CdSO_4 \cdot 200H_2O$	5	0.0000090	0.00268	0.00747	0.01115	0.01107	387	391
$CdSO_4 \cdot 200H_2O$								
$CdSO_4 \cdot 400H_2O$	6	0.0000095	0.00283	0.00234	0.00517	0.00496	98	108
2 3	7	0.0000236	0.00703	0.01565	0.00268	0.02211	697	722
5 6	8	0.0000185	0.00551	0.01082	0.01633	0.01603	485	499

Table IV. gives the results of thirteen different cells. As before 2 and 3 should equal 1, and 5 and 6 should equal 4. While the agreement is quite satisfactory, it is not so good as for the zinc sul-

phate. It will be seen that for all but one, 1*c*, of the thirteen cells, the computed E.M.F. exceeds the observed value; the difference between the two being about 2 per cent. It is further to be noted that this difference is comparatively constant, indicating an experimental error, rather than some defect in the principles involved.

The heat of dilution accounts for from fifty to eighty per cent. of the total E.M.F. of the cell.

Zinc Chloride Cells.

In the preceding experiments the cells have a positive heat of dilution and a positive temperature coefficient. Three other variations may arise, namely, (1) a positive heat of dilution with a negative temperature coefficient; (2) a negative heat of dilution with a positive temperature coefficient; (3) a negative heat of dilution with a negative temperature coefficient. In the third case the E.M.F. would be reversed, that is, the electrode in more dilute solution would become the cathode. In the other two cases the direction of the E.M.F. depends upon the relative magnitude of the quantities. For the solutions used the zinc chloride cell satisfies case (1) — a positive heat of dilution with a negative temperature coefficient — and will be next studied.

Upon diluting zinc chloride solutions hydrolysis takes place causing a change in concentration. The addition of the amalgam electrode sometimes brings about this change; even a change in temperature may produce it. Taking these things into account, it is difficult to prepare a solution of known concentration and to maintain it throughout the test.

The amalgam for this cell was a portion of that originally prepared for the zinc sulphate cells, and diluted to about one per cent. Solutions of approximately $ZnCl_2 \cdot 20H_2O$ and $ZnCl_2 \cdot 400H_2O$ were used for the preliminary tests. These were carefully filtered, then subjected to temperature changes and refiltered. Cells from these solutions remained reasonably constant but were not entirely free from hydrolysis (especially the more dilute solution) when subjected to temperature changes. The observed E.M.F. was higher than the computed value; this was probably due to the fact that the dilute solution hydrolyzed, thereby decreasing its concentration.

After trying solutions of different concentration under various conditions it was found that hydrolysis could be avoided by allowing the solutions to stand for some time; accordingly the two solutions from which the final determinations were made, $ZnCl_2 \cdot 18.84H_2O$ and $ZnCl_2 \cdot 180H_2O$, were allowed to stand for about six weeks. These solutions were carefully filtered before using. Great care was taken that all parts of the cell were perfectly dry and the solutions made contact in the middle of the filter paper plug in the connecting tube. Table V. gives the readings of the cell with these two solutions.

TABLE V.

Date.	Cell Set Up.	Temp.	E.M.F.
August 3,	5:00 P. M.	25	0.06737
" 4,	8:00 A. M.	25	0.06722
" 4,	8:45 "	25	0.06722
" 5,	9:00 "	25	0.06722
" 5,	3:00 P. M.	25	0.06720
" 6,	8:30 A. M.	25	0.06718
" 6,	11:30 "	25	0.06717

The total change, after equilibrium had been reached, was only 0.00005 volt. During this time, the temperature was lowered to 0° twice, and raised to 40° three times. The concentration of the solution was determined by titration against $AgNO_3$ using potassium chromate as an indicator. Heats of dilution were obtained by interpolation by means of a curve plotted from Thomsen's values. The curve as shown in Fig. 2 appears perfectly smooth, and when plotted on a large scale gives values which can be but little in error. To insure greater accuracy the solutions chosen were approximately those for which the heats of dilution had been determined.

Table VI. gives the results of three different cells from these solutions.

TABLE VI.

Solutions.	Cells.	dE/dT	$T \cdot dE/dT$ at 25°.	E'_{25}	Comp. E.M.F.	Obs. E.M.F.	Comp. Heat of Dil. Cal.	Obs.[1] Heat of Dil. Cal.
$ZnCl_2 \cdot 18.8H_2O$	*a*	−0.000097	−0.02891	0.09832	0.06941	0.06722	4429	4530
$ZnCl_2 \cdot 180H_2O$	*b*	−0.000098	−0.02920	0.09832	0.06912	0.06723	4443	4530
	c	−0.000097	−0.02891	0.09832	0.06941	0.06712	4435	4530

[1] Thomsen (see Table IX.).

The agreement is very satisfactory, and as in the case of the cadmium sulphate cells, the computed E.M.F. is greater than the observed value.

The zinc chloride cell furnishes a specially instructive illustration of the correctness of the principle involved, because the temperature coefficient is negative, as in most voltaic cells. The E.M.F. is accordingly less than the value derived from the heat of dilution.

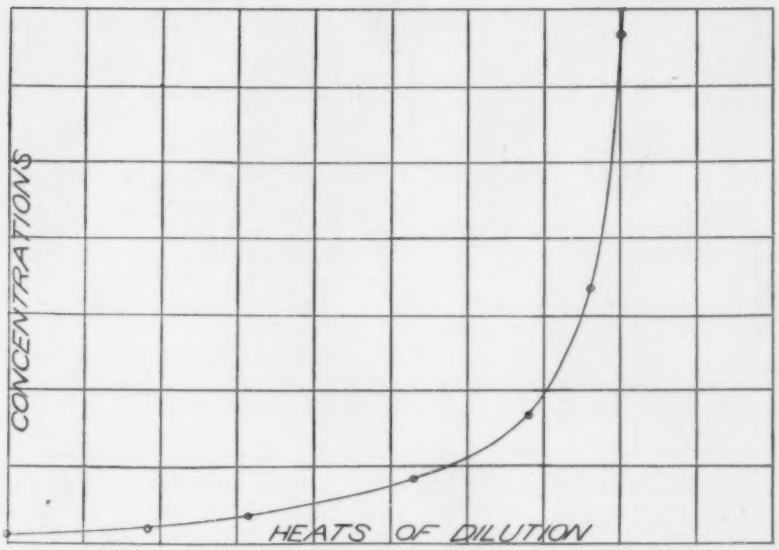

Fig. 2.

Lead Nitrate Cells.

Two more possible variations remain — a negative heat of dilution with either a positive or negative temperature coefficient. It becomes therefore a matter of great interest to know if the Gibbs-Helmholtz principle will apply to these. The lead nitrate cell fulfills one of these conditions, a negative heat of dilution with a positive temperature coefficient.

The solutions for this cell were prepared by weight from the recrystallized salt, similar to the sulphate; the amalgams, electrolytically, from an acid solution of the purified salt, and they were kept under an acid solution. Lead amalgams when left exposed to the air or in contact with aqueous solutions oxidize readily.

As a preliminary step, tests were made with reference to the constancy of the electrodes. With dilute amalgam and concentrated solutions the cell remained fairly constant, but when dilute solutions were used the readings were more variable. The electrodes in the dilute solutions became covered with a grayish film probably due to oxidation. Tests were made with $Pb(NO_3)_2 \cdot 400H_2O$, the most dilute solution used, to determine under what conditions oxidation might be prevented. It was found that by slightly acidulating the solution with nitric acid the film did not form and the readings became reasonably constant. Next, this test was extended to see what effect the acid had upon the initial readings of the cell. Equal portions of the two solutions from which the cell was set up were

TABLE VII.

Solutions.	Cells.	dE/dT	$T \cdot dE/dT$ at 25° C.	E_h	Comp. E.M.F.	Obs. E.M.F.	Comp. Heat of Dil.	Obs.[1] Heat of Dil.
$Pb(NO_3)_2 \cdot 100H_2O$	*a*	0.000146	0.04351	−0.02756	0.01595	0.01620	−1659	−1270
$Pb(NO_3)_2 \cdot 400H_2O$	*b*	0.000145	0.04321	−0.02756	0.01565	0.01632	−1240	−1270
	c	0.000141	0.04202	−0.02756	0.01446	0.01636	−1183	−1270

treated with the same quantity of nitric acid. The amount used was just enough to prevent the film from forming, and was determined beforehand. To make certain that both solutions were treated with the same amount, the conductivity water from which the solutions were made was acidulated before preparing the solutions. Such cells gave concordant values with change of temperature and remained reasonably constant. Furthermore, the readings were almost identical with the initial readings when no acid was used. For example, a cell without acid started with 0.01616 volt and reached apparent equilibrium at 0.01630 volt in about two hours, after which it slowly dropped in value. Table VII., which embodies the result of the final test, shows that this is in exact agreement with the mean of the three cells examined. Thus it is fair to suppose that the addition of the nitric acid did not affect the initial readings. It might be noted in this connection that all cells without the acid attained about the same initial readings at apparent equilibrium, and then slowly dropped in value. Constant agitation seemed to lessen this change, but did not completely eliminate it.

[1] Thomsen (see Table IX.).

Referring to Table VII., it will be noted that the computed E.M.F. is now less that the observed value. This was found to be true for all the preliminary determinations. The difference between the computed and observed values in cells *a* and *b* is well within the limits of experimental error. No reason can be assigned for the greater variation in cell *c* as it gave a good initial reading and remained fully as constant as the others.

Referring again to comparisons by percentage difference, it might be pointed out that if $T \cdot dE/dT$ observed be compared with $T \cdot dE/dT$ computed the percentage difference is only about one third of what it is for the E.M.F.'s and less than two thirds of what it is for the heats of dilution. For example, take cell *a*, $T \cdot dE/dT = 0.0435$ volt; $T \cdot dE/dT$ computed $= 0.04373$ volt; percentage difference is 0.5. The percentage difference between the observed and computed E.M.F. is about 1.4; between observed and computed heats of dilution, 0.8. The observed and computed E.M.F.'s do not give a fair comparison of the quantities involved unless the temperature coefficient and heat of dilution are both of the same sign.

This last case is particularly interesting since the chemical process is endothermic and the cell when in operation uses only a portion of the heat absorbed from the surroundings to be converted into electrical energy. It furnishes a striking proof of the incorrectness of the assumption that the heat of reaction is a measure of the electrical energy of a cell.

Discussion of Results.

One more variation remains — a negative heat of dilution with a negative temperature coefficient. As previously stated such a cell must have its E.M.F. reversed. This combination does not seem probable, for taking a current from such a cell would increase the difference in concentration of the solutions, thereby causing its E.M.F. to rise.

However, as it is, the results obtained are a very satisfactory confirmation of the principle involved. The deviation from the computed value in each case is comparatively constant indicating experimental errors. It now becomes a matter of interest to attempt an explanation of the probable cause of these small discrepancies.

The last term of the equation $T \cdot dE/dT$, is proportional to the absolute temperature, and therefore purely thermo-electric. According to Carhart's thermo-electric theory, the coefficient dE/dT is the algebraic sum of all the thermo-electric forces per degree arising at the several junctions. The temperature between the junction of the two liquids was considered the same as that at the electrodes. This perhaps is not strictly true because there would be more or less diffusion between the two solutions and the construction did not admit of immersing the whole cell. The thermo-electromotive force at the junction is accordingly less than the value which would be obtained with the junction at the same temperature as the electrodes. This assumption that the temperature of the junction is not always the same as that of the electrodes, and furthermore that it is variable, is borne out by the fact that the cells always remained the most constant at 25° or about room temperature. Results based on this assumption would indicate that for the zinc sulphate cell the thermo-electromotive force at the junction was practically negligible; for the cadmium and zinc chloride cells, it was directed from the concentrated to the more dilute solution; and in the lead nitrate cell, from the dilute to the more concentrated solution.

Secondly, the small difference may be explained on the assumption that the electrode in the more dilute solution oxidized to a greater extent than the other, thus establishing a counter E.M.F. In the case of the lead nitrate the observed E.M.F. is higher than the calculated value, which would indicate the reverse had taken place. This may be caused, however, by the addition of the nitric acid affecting the surface condition of the electrodes.

Thirdly, this difference between the observed and computed values may be due to the calorimetric determination of the heats of dilution. The heats of dilution as given may be inaccurate and are in need of revision because of modern facilities and a better knowledge of absolute units. Assuming the Gibbs-Helmholtz equation to apply rigorously in all cases, the results would indicate that the heats of dilution for the zinc sulphate solutions are correct as determined, that the heats of dilution for the cadmium sulphate and zinc chloride solutions are too large, and that the heats of dilution for the lead nitrate solutions are too small.

SUMMARY.

1. Simple concentration cells, made up of various solutions for which the heats of dilution have been determined, were investigated with reference to the application of the Gibbs-Helmholtz equation. The total heat of reaction becomes the heat of dilution and answers for the first term of the equation.

2. The four following cells were investigated: (1) Cadmium amalgam electrodes with cadmium sulphate of different concentration as electrolytes; (2) zinc amalgam electrodes with zinc sulphate of different concentration as electrolytes; (3) zinc amalgam electrodes with zinc chloride of different concentration as electrodes; (4) lead amalgam electrodes with lead nitrate of different concentration as electrolytes.

TABLE VIII.

Solutions.	E_h	$T \cdot dE/dT$	Comp. E.M.F.	Obs. E.M.F.	Comp. Heat of Dilution.	Obs. Heat of Dilution.
$ZnSO_4 \cdot 50H_2O$—						
$ZnSO_4 \cdot 400H_2O$	0.00178	0.01535	0.01713	0.01709	80 Cal.	82 Cal.
$CdSO_4 \cdot 30.6H_2O$—						
$CdSO_4 \cdot 400H_2O$	0.01565	0.00693	0.02258	0.02211	701 "	722 "
$ZnCl_2 \cdot 18.8H_2O$—						
$ZnCl_2 \cdot 180H_2O$	0.09832	−0.02901	0.06931	0.06719	4435 "	4530 "
$Pb(NO_3)_2 \cdot 100H_2O$						
$Pb(NO_3)_2 \cdot 400H_2O$—	0.02756	0.04336	0.01580	0.01626	−1250 "	−1270 "

3. A filter paper plug in the connecting tube was used to prevent the mixing of the two solutions and to reduce diffusion to a minimum.

4. A method was found for successfully preventing oxidation of the lead amalgams under lead nitrate solution without vitiating the values of the readings of the cell. Zinc chloride solutions were also used without hydrolysis.

5. Table IX. gives a brief summary of the four cells investigated. For the lead nitrate cell the mean of cells *a* and *b* only are used.

The first cell has a large positive temperature coefficient with a relatively small heat of dilution; the second, a small temperature coefficient with a relatively large heat of dilution; the third, a nega-

tive temperature coefficient with a large positive heat of dilution; the fourth, a positive temperature coefficient with a relatively large negative heat of dilution. Of the two variables E_h and $T \cdot dE/dT$ which go to make up the E.M.F. of the cell, three of the four possible variations worked out.

6. The Gibbs-Helmholtz equation applies rigorously in all cases, the difference being less than the probable experimental error.

TABLE IX.

m	$ZnSO_4$ n 20	$CdSO_4$ n 30.6	$ZnCl_2$ n 5	$Pb(NO_3)_2$ n 40
10			1850	
20			3150	
50	318	223	5320	
100	367	443	6810	−1230
200	385	614	7630	−1980
400	400	722	8020	−2500

In conclusion the writer wishes to express his thanks to Professor Carhart under whose direction this investigation was conducted for his interest and helpful suggestions.

For convenience of reference a table of the heats of dilution for the solutions used is appended. The heats of dilution are given in gram calories. m is the number of gram-molecules of water added to the solution when it already contains n gram-molecules of water to one gram-molecule of the anhydrous salt.

UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.,
May, 1909.

ANODE DROP WITH HOT CaO CATHODE.

By C. D. Child.

THE drop in potential at the anode of the electric arc in a vacuum has been found to be much smaller than the corresponding drop in a vacuum with small currents and unstriated discharge. The value of the former is about 6 or 7 volts,[1] while that of the latter is about 20 volts.[2] The discharge from hot CaO in a vacuum is in some respects intermediate between these two forms of discharge and the investigation of which the following is an account was undertaken for the purpose of examining this drop with such intermediate currents.

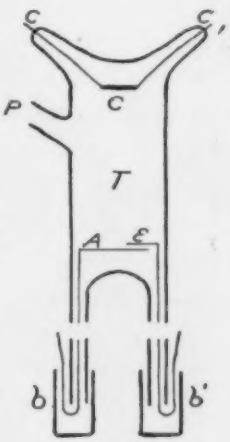

Fig. 1.

Apparatus. — The apparatus in the first experiments here described is shown in Fig. 1. T is a tube 3 cm. in diameter, through which the discharge passes. C is the cathode consisting of a piece of platinum foil, approximately 2 mm. in width, 6 mm. in length and .02 mm. in thickness, the bottom being covered with CaO. This was welded to aluminum wires and was heated by a storage battery connected at c and c'. A is the anode. This was an iron disk 2.4 cm. in diameter, soldered to an iron wire which ran through a tube containing mercury into a cup b. The wire was there bent and brought out of the cup. By this means the anode could be conveniently raised and lowered, while the air was exhausted from the tube. The potential difference between A and C was maintained by a battery of small storage cells. e is the exploring electrode brought out at b' in a similar way.

[1] Wills, Phys. Rev., 16, 65, 1904. Child, Phys. Rev., 20, 365, 1905. Stark, Retschinsky and Schaposchihnoff, Ann. d. Phys., 19, 243, 1905. Pollak, Ann. d. Phys., 19, 217, 1906.

[2] Skinner, Phil. Mag. (6), 8, 387, 1904.

This was also iron. The upper vertical part was covered with a small glass tube for several centimeters, in order to insulate this part of the wire from the conducting gas about it. The wire was .4 mm. in diameter. The length of the horizontal part was 4 mm. (Experiment showed that this length might be varied greatly without affecting the readings.) P is the connection to the vacuum pump, McLeod gauge, and tube containing P_2O_5. e was connected to a quadrant electrometer which was standardized by comparison with a Weston voltmeter. The current through the tube was measured by a Weston ammeter, or when too small for that instrument, by a galvanometer which was compared with the ammeter. The part of the tube containing the cathode and the leading-in wires was a separate piece of glass which was sealed into the other tube with sealing wax. This enabled one to replace the platinum foil in case it was melted.

Anode Drop with Different Distances between Electrodes. — The first experiment given below is a repetition of one given by Skinner,[1] showing the relation between the anode drop and the distance between the electrodes. In this the current through the tube was kept as nearly as possible at 1.4×10^{-4} ampere, and the pressure at .035 mm. of mercury. The distance between A and e was approximately 1 mm. and slight variations of this distance made no appreciable difference in the readings. The gas in these experiments was air. The current remained practically constant as long

TABLE I.

Distance Between Electrodes in cm.	Anode Drop in Volts.	Remarks.
.5	23	In Crookes dark space.
1	15.5	" " " "
2	14.5	" " " "
3	5.5	In negative glow.
4	6	" " "
6	9	" " "
7	21	Faint glow on anode.
8	21	" " " "
9	25	Glow on anode.
10	13	First striation extending 1.5 cm. above anode.

[1] Phil. Mag. (6), 2, 637, 1901.

as the temperature of the cathode was constant, irrespective of the distance between the electrodes. One hundred cells of a storage battery were used in series with a water resistance of approximately 2,000 ohms. The data found are given in Table I.

These data are plotted in Fig. 2. The large values of the anode

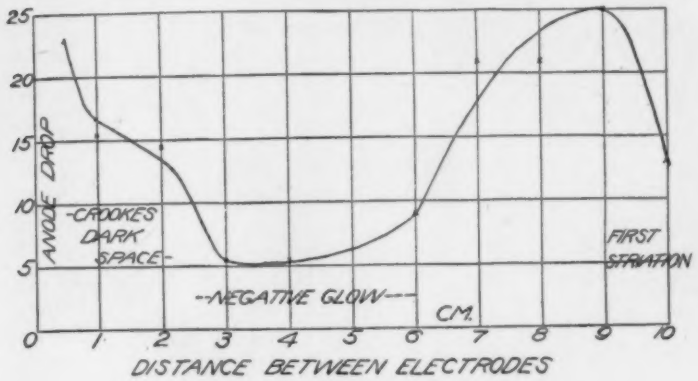

Fig. 2.

drop occurred in Crookes dark space and just before a new striation began to appear. This was quite in harmony with what was found by Skinner.

In addition it was found that increasing either the current or the pressure of the gas shortened the Crookes dark space greatly. This is shown by comparing the preceding table with the data given in Table II., where the current was .011 ampere and the pressure .07 mm. of mercury.

TABLE II.

Distance Between Electrodes in cm.	Anode Drop in Volts.	Remarks.
.5	5.5	In negative glow.
1	3.6	" " "
2	3.5	" " "
4	3.7	" " "
6	3.7	" " "
7	4.4	" " "
8	3.4	" " "
9	17.5	Beginning of bright glow.
10	16.5	One cm. of glow appearing above anode.

The curve given by these data is plotted in Fig. 3.

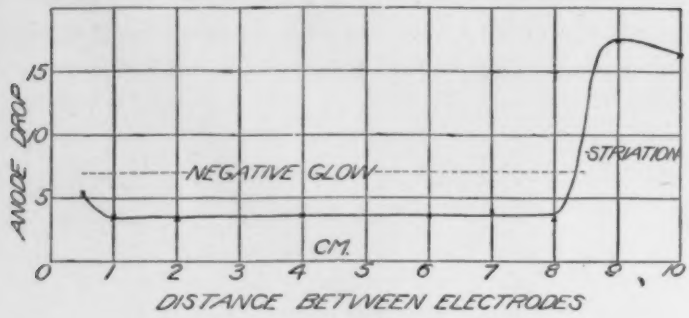

Fig. 3.

Anode Drop and Striation. — It was found also that the anode drop varied as the position of the anode in the striation was varied. In order to show this well by having wide striations, a very low pressure was necessary, and with the tube used in the preceding experiment it was not possible to get all of a striation at such a low pressure, except when the cathode rays were deflected to the side of the tube by a magnet. Bringing a magnet near to the discharge is equivalent for the purpose in hand to lengthening the tube. The following observations were, therefore, taken with changes in position of striation produced by changing the position of a magnet. The distance between the electrodes was 8 cm. The pressure was .019 mm. and the current was constant at .022 ampere.

Table III.

Anode Drop in Volts.	Remarks.
6.4	No glow at anode. No magnetic field.
19	Faint glow appearing at anode as magnet is brought nearer.
16	Top of glow 8 mm. above anode.
13	" " " 12 mm. " "
12	" " " 18 mm. " "
12	" " " 25 mm. " "
12	" " " 30 mm. " "
18	" " " 35 mm. " " Second dark space at anode.
17	Second glow 8 mm. above anode.

These data are plotted in Fig. 4. The fact is here more clearly

shown that the largest value of the anode drop was at the end of the dark region just as a faint glow was about to appear on the anode. Many cases of this sort were examined in the course of the investigation and this was found to hold true in all cases.

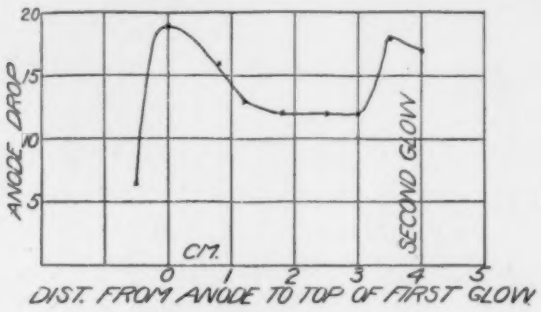

Fig. 4.

Anode Drop with Different Currents. — Data are given in Table IV. for the anode drop with different currents. The distance between the electrodes was 5 cm. The pressure of the gas was .15 mm. The other conditions were the same as in the preceding experiments. The current was varied by changing the temperature of the cathode.

TABLE IV.

Current in Amperes $\times 10^{-3}$.	Anode Drop in Volts.	Current in Amperes $\times 10^{-3}$.	Anode Drop in Volts.
.01	34	2.5	3.3
.02	26	9	4.6
.034	8	20	7
.051	5	250	14
.10	3.5	500	18
.60	2.5	700	20
.95	2.2		

Part of these data are plotted in Fig. 5. With the two smaller currents the only luminosity was a faint glow about one third of the way from the anode to the cathode. With larger currents this appeared to rise toward the cathode. With currents larger than those given in the table the beginning of a striation appeared on the anode.

The form of this curve was changed greatly by changing either the pressure of the gas, or the distance between the electrodes. It was apparently impossible to repeat the series of observations and get the same values, because the cathode continually gave out a slight quantity of occluded gas. However, the general character of the curve was always the same. There were always large values of the anode drop with very large and with very small currents.

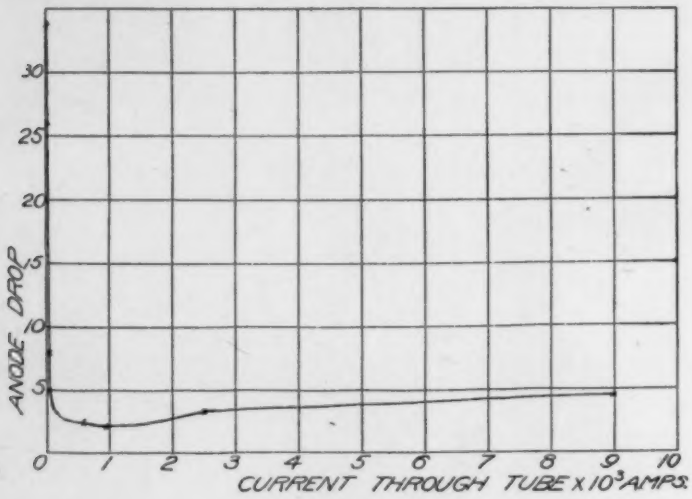

Fig. 5.

Larger values of the current approach those which may be had with the mercury arc and these will be considered in a later part of this article.

Anode Drop in Magnetic Field. — It would appear from what has preceded that the anode drop depended largely on whether the anode was in the direct path of the cathode rays or not. This was perhaps shown more clearly by deflecting the rays by means of a magnet. The change thus produced was especially noticeable when the anode was placed so that without the magnet the anode drop was small, as is shown in the following table.

Deflecting the rays by a magnet is equivalent to moving the anode further from the cathode as has been stated, but it is instructive to show the experiment in this form. In the following table the first reading is that given when there was no magnetic field. In

each succeeding one the magnet was moved nearer. The number of cells was 120. The distance between the electrodes was 8 cm. The pressure was .008 mm., and the temperature of the cathode remained constant.

TABLE V.

Current in Amperes $\times 10^{-4}$.	Anode Drop in Volts.
1.95	2.4
2.05	9.3
2.07	18
2.14	23

Anode Drop and Path of Cathode Rays.— That this increase in the anode drop was caused by the deflection of the cathode rays and not by any direct effect of the field was shown by taking the cathode out of the tube T and placing it in a side tube, which was made to open into T two or three centimeters above e. It was so placed that under ordinary conditions no rays could go directly to the anode. When this occurred there was a glow above the anode at all pressures which could be attained. The lowest pressure was .001 mm. and the least drop was 22 volts.

By placing a magnet near the tube and in the right position the cathode stream could be made to curve down into the tube T, so as to strike directly on A. Under such conditions the glow disappeared and the anode drop decreased to 2.6 volts, while the current remained practically constant.

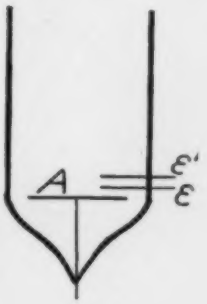

Fig. 6.

Anode Drop and the Electric Force near the Anode. — Skinner[1] calls attention to the fact that the region between the cathode and the first striation, where the anode drop is greatest, is also that where the electric force is greatest. It was found, however, on examining this force experimentally, that this statement would not hold under all conditions. In making measurements on this point the lower part of the tube was replaced by one shown in Fig. 6. A is the anode as before, e and e' are two exploring electrodes brought through the side of the tube, the distance between them being 1.2 mm. These could not be moved, but since the different parts of the discharge

[1] Phil. Mag. (6), 2, 621, 1901.

could be brought to the anode either by changing the current or by bringing a magnet near the tube, this arrangement was considered sufficient. The distance between the electrodes was 10 cm.

The fact that the anode drop was not always greatest when the electric force was greatest was best shown by changing the current from quite small to very large values. This was done by changing the temperature of the cathode. There is given in Table VI. a series of readings taken in this way.

TABLE VI.

Current Through Tube in Milliamperes.	Anode Drop in Volts.	Potential Difference Between e and e' in Volts.
.007	18	+2.6
.035	4.4	− .4
.7	4.4	− .25
2.7	5	− .25
112	24	−2.0
112	15	+2.5

The two last readings were taken with the same current, but in the last one a magnet was brought near the tube, causing the top of a striation to appear two or three millimeters above the anode.

The negative sign before some of the values in the third column indicates an electric force in the opposite direction to that in which the current was flowing. Very careful tests indicated that a force existed at times in such a direction. The current is carried against this by the momentum of the negative ions.

A very great change in the elecric force took place between the first and second readings, while the change in the anode drop was small. Between the second and third a large change took place in the anode drop while the change in the electric force was small.

A similar lack of agreement in the changes was found as a striation was about to appear. This, however, is less significant, since the electric force changes very rapidly at the beginning of a striation and the electric force measured by the electrodes may have been quite different from that between the lower electrode and the anode. However, this objection can hardly hold in the case of the first three readings, so that we have good reason for saying that the anode drop does not depend on the electric force in its neighborhood.

The conductivity of the gas in the neighborhood of the anode

was also examined. This was done by placing the two electrodes e and e' parallel to the anode and connecting them to an E.M.F. of about 20 volts and to a galvanometer. The conductivity increased quite rapidly with increase of current and seemed to depend but very little on whether there was a glow at the anode or not. If the conductivity was measured when there was no glow at the anode and a glow was then produced by bringing a magnet near the tube, the conductivity changed but very little, while the anode drop changed greatly under these conditions. In fact no relation could be found between the anode drop and the conductivity of the gas near the anode. This was found to be true both with iron and with mercury for the anode.

Anode Drop with Higher Pressures. — As the pressure of the gas was increased there came to be a glow at the anode at all times, whether it was a dark or bright part of the striation. The variations of the anode glow were then much smaller than those given above.

At still higher pressures there were no striations and no glow except in the immediate neighborhood of the electrodes. Under these conditions the anode drop scarcely varied at all when the current was changed. It did, however, increase as the pressure of the gas increased. Thus when the distance between the electrodes was 6 cm. the anode drop changed from 19.5 volts when the pressure was .2 mm. to 23 volts when it was 2 mm. This increase was approximately proportional to the increase in pressure. With these higher pressures the luminous discharge could not be started with the 160 cells used, except by passing a spark through the tube from an induction coil. At the higher pressures there was no change in the anode drop which could be detected when the current through the tube was varied.

With hydrogen in the tube it was possible to have a discharge with greater pressures and this increase in the anode drop with increase in the pressure was then still more noticeable. Thus it increased from 10.5 volts when the pressure of the hydrogen was 1.2 mm. to 28.5 volts when it was 5.3 mm. At this pressure it varied approximately .7 volt as the current was changed, there being a minimum value when the current was .003 ampere. This

variation was similar to that shown in Table IV., except that the value of the anode drop was here much larger. The distance between the electrodes was here 9 cm.

Anode Drop in Hydrogen. — The anode drop was also examined with the discharge through hydrogen using iron for the anode, and it was found to have the same general characteristics as that with the discharge through air. The currents which passed through the tube were larger than those which passed under the same conditions with air. The disappearance of striations occurred with greater pressures and it was possible to pass the discharge with greater pressures, but the anode drop showed the same dependence on the condition of ionization in the tube, and has approximately the same values.

Anode Drop with Mercury and Aluminum Anodes. — These experiments were repeated with mercury for the anode instead of iron. A film always formed on the surface of the mercury when a glow appeared in the tube and this made the anode drop somewhat greater. For the purpose of keeping a fresh surface on the mercury, the bottom of the tube shown in Fig. 6 was replaced by a long tube running into a cistern of mercury, which was open to the air. When the surface became coated, the cistern was lowered a few centimeters and then raised, bringing a comparatively clean surface of the mercury to the top. With such a surface the anode drop was, as nearly as could be determined, the same as with iron.

With an aluminum anode the anode drop was found to be much larger than with iron, although it showed the same general characteristics. The higher values for aluminum quite agree with those found by Skinner.[1]

No further comparison of the drop with different metals was made, since it is necessary to have much more complicated apparatus in order to make accurate comparisons.[2]

Large Currents Through Tube. — None of the currents used in the preceding experiments approach in size those of the ordinary form of electric arc. While it is possible to get such currents, it is difficult to maintain them long enough to secure satisfactory measurements.

[1] Wied. Ann., 68, 757, 1899.

[2] See Phil. Mag. (6), 8, 387, 1904.

Three different substances were used for heating the CaO when attempting to get large currents, namely, platinum, tungsten and carbon. It was possible to get momentary currents as large as 1.5 amperes with the platinum foil, but in every case the foil was melted before measurements with the anode drop could be made, but as far as could be observed the discharge was similar to that in the preceding experiments. There were striations and the anode drop was in the neighborhood of 20 volts.

The tungsten wire which was used in these experiments was very kindly furnished by the General Electric Company. It was .32 mm. in diameter. It was possible with this to get larger currents through the tube, but they were nearly as transitory as when the lime was heated on platinum. In this case the trouble was due to the vaporization of the CaO. At higher temperatures it was entirely vaporized, leaving the tungsten as bright as when new.

Before this point was reached the CaO appeared to melt and collect in globules on the cooler parts of the wire. For some reason which I have not discovered, it was more difficult to secure the glow from CaO on tungsten than on platinum. It appeared to be necessary to raise the temperature of the tungsten every few seconds in order to maintain the discharge. The wire also gave out occluded gases in much greater abundance than platinum, so that it proved much less satisfactory than platinum for the smaller currents through the tube, and not any more satisfactory for the large ones.

The carbon also gave out a large amount of occluded gas and the CaO was driven off from this at higher temperatures, but it proved more satisfactory than either of the other substances for large currents. The carbon used was 1.6 mm. in diameter and the current passed through it was approximately 18 amperes. The current through the tube was furnished by a 110 volt dynamo, and was regulated by resistance in series with the dynamo. The tube was 2 cm. in diameter and the distance from the cathode to anode was 6 cm.

It was found that with currents in the neighborhood of .7 ampere a change occurred in the appearance of the anode. The glow then became concentrated in two or three spots and the anode drop became smaller. With currents in the neighborhood of 1 ampere the glow was confined to one spot and this was quite luminous.

The striations then became indistinct or disappeared entirely and the anode drop became still smaller. This change from the form where there was no concentration of the glow at the anode to the one where there was but one spot of light was liable to occur without any intermediate condition.

With this change the potential difference between the cathode and the anode became smaller and the current became much larger. In other words the discharge had become an arc. When the change had occurred resistance could be inserted in the circuit and the current lowered a considerable extent without changing back to the striated form.

A series of readings showing the relation between the current and the anode drop is shown in Table VII. The pressure of the gas was approximately .013 mm. These are only approximate values, for the carbon was continually giving out gas and the anode drop was largely affected by the amount of gas present.

TABLE VII.

Current Through Tube in Amperes.	Anode Drop in Volts.	Remarks.
.2	19.3	No concentration of glow at anode.
.7	15	Three bright spots at anode.
1.2	12	One bright spot at anode.
2	10	" " " " "
2.3	9.8	" " " " "
3	8.2	" " " " "

The discharge from CaO on carbon was also tried through a larger tube, one 3.5 cm. in diameter and it was found that there was no change in the form of discharge, until the current was more than one ampere, and then it suddenly changed to the arc form with a current of 5 amperes.

These experiments were with a mercury anode. Similar phenomena were observed with iron and carbon anodes. With the carbon different sizes and lengths were used and it was found that the larger the surface of the carbon exposed, the larger the amount of current flowing when the change from the striated to the arc form occurred. Apparently the point where this change occurs depends on the density of the current rather than on the total current.

The attempt was also made to use the luminous vapor rising

from the mercury arc as a source of negative ions. This was largely a repetition of the work of Pollak[1] but it seemed worth while to go over the work again with the knowledge of the preceding experiments in hand. It would seem at first sight as if this method would easily afford an opportunity to pass from small to very large currents by continuous changes and without trouble caused by the vaporization of CaO or by change of pressure due to occluded gas. But other difficulties made it harder to secure constant results by this means than by the hot lime on carbon. As has been shown in a preceding article[2] the luminous vapor rising from a mercury arc is highly conducting and the part of this in the boundary between the hot mercury vapor and the residual gas in the tube is the most conducting of all. This is an excellent source of negative ions but it is continually moving, so that it is impossible to keep the conditions steady.

In the second place the pressure in the vapor arising from the arc is much higher than in the remaining part of the tube and with the increase in pressure the striations become less distinct. The pressure appears also to be continually changing. As a result of both of these and possibly of others the striations were not nearly as distinct as with hot lime, and it was impossible to get any satisfactory measurements by this means.

It was evident that the discharge in this case went through the same general changes as with the discharge from hot lime. There were striations which changed with larger currents into a continuous glow with a concentration of the glow at one point on the anode. With this concentration there was a decrease in the anode drop as with the other case.

The lowest anode drops with the arc in a vacuum occur when the anode is in the direct path of the cathode rays, as has been pointed out by Stark, Retschinsky and Schaposchnikoff.[3] This was the cause of the low anode drop found by myself in a preceding article.[4] This condition is quite distinct from that given above, where there is a concentration of the current at one point, but is probably identical

[1] Ann. d. Phys., 19, 239, 1906.
[2] PHYS. REV., 22, 221, 1906.
[3] Ann. d. Phys., 18, 213, 1905.
[4] PHYS. REV., 20, 365, 1905.

with that in the preceding work where the anode was in the direct path of the cathode rays.

Explanation of the Variation in the Anode Drop. — The anode drop is due primarily to an excess of negative ions in the immediate neighborhood of the anode. Negative ions come to the anode from the gas, and if no positive ions come from the anode, there must of necessity be an excess of negative ions in its neighborhood. Evidently this excess will be smaller for a given current the greater the velocity of the negative ions moving through this region. It will also be smaller, if positive ions come from the metal or are produced at the surface of the anode. Some of the phenomena mentioned above appear to depend on the velocity of the negative ions as has been pointed out by Skinner; others on the production of positive ions at the surface of the anode.

In saying that the anode drop depends on the velocity of the negative ions, one must remember that the average velocity of the ions is meant. Not only the velocity of the cathode rays but also that of the negative ions produced in the gas between the electrodes must be considered. No quantitative explanation of this drop can be tested until the average velocity of the negative ions in the immediate neighborhood of the anode can be measured. It is, however, evident that the lowest anode drop occurred where we should expect this velocity to be greatest. Thus we should expect the velocity of the cathode rays a few centimeters from the cathode to be great and in this region the anode drop is indeed small as was shown in Table I.

As this distance is increased the ions coming from the cathode and having high velocity are stopped by collision. Others are produced by these collisions and, since the field where they are produced is weak, the velocity which is given to them is small, so that the average velocity of the ions is diminished. This is the region just above a striation and here we find the anode drop to be large.

When the velocity of the negative ions has become very small, they are crowded together and a strong field is produced beyond them. Why there should be this periodic change in the field is not known, and we can here only take account of the fact that it exists. Where the field again becomes strong, the velocity of the negative

ions is again large. This is the region of the luminous part of a striation and here again we find the anode drop to be smaller.

This is true whether the cathode rays are stopped by collision with other molecules or by hitting the side of the tube, as when deflected by a magnet, or when the cathode was placed in a side tube. In any case we have the formation of a striation and a rise again of the anode drop.

As one passes downwards through the striation the negative ions are again stopped and others produced, which move more slowly, since they are in a weak field. In this region again we find the anode drop to be greater.

That the negative ions produced in the tube, or secondary cathode rays as one might call them, go for some distance through the gas before being stopped, was shown by a phenomenon which was noticed when the cathode was in a tube at right angles to the main tube. With this arrangement the top of the striation was concave downward and there was a conical region immediately under this which was brighter than the rest. That this was caused by the projection of rays from the top of the striation was shown by changing the current through the tube. As the current was decreased the top became more concave and the cone of light was brought to a focus nearer to the top.

The cone of light could also be deflected by a magnet and the direction in which it was deflected was the correct one for cathode rays. The length of this cone was about 2 cm. A similar phenomenon could at times be detected when the cathode was above the anode, but the striation was then flatter and the cone could not then be readily detected.

At first sight this explanation appears to fail when the electrodes are near together, for there we should expect to find the velocity of the negative ions large and the cathode drop to be small, while in fact the anode drop was here large. However, Skinner called attention to the fact that with short distances between the electrodes more cathode rays are reflected. Whether we are to consider the cathode rays as being reflected, or as producing secondary rays, there is in either case a large number of negative ions flying away from the anode. These would increase the density of negative elec-

tricity near the anode. Or looking at it from another standpoint, a larger drop in the neighborhood of the anode would be necessary to draw back again these negative ions to the anode. There was evidence that more cathode rays were reflected when the electrodes were near together in the fact that then the part of the tube above the cathode was more luminous, as if rays were reflected from the anode into that region.

With very small currents the only luminosity was in the lower part of the tube near the anode. One might, therefore, expect that a greater number of ions would be formed in that region and would have less velocity when they came to the anode. This would make the anode drop large, as it was indeed found to be.

In what has preceded no account has been taken of ionization at the surface of the anode, such as might be produced by the impact of negative ions. While such ionization may occur at low pressures, there was apparently no evidence of it. At higher pressure it would, however, appear to be the controlling factor. With pressures in the neighborhood of a millimeter, there was no glow in the region between the electrodes, but there was one at the anode with all distances and currents. The anode drop was then quite constant, scarcely varying at all with change of current and increasing but slowly with increase of pressure. Apparently under these conditions the drop at the anode gives the negative ions sufficient velocity to ionize the molecules at the surface of the anode, or else in its very immediate neighborhood, irrespective of what their velocity may have been before reaching the anode. When this critical velocity was reached, changes in the current or in other conditions would have but small effect, for if any change should momentarily increase the anode drop, there would immediately be an increase in the number of positive ions produced at the surface of the anode and this would again lower the anode drop.

With currents in the neighborhood of .5 ampere the decrease in the anode drop appears to be quite analogous to that which occurs in the electric force in a vacuum tube with much smaller currents. With very small currents from hot lime the electric force through the tube may be large. As the current is increased the conductivity of the vapor is greatly increased and the electric force through

the vapor decreases. Whether this is caused by the high temperature of the gas or by the repeated bombardment of an atom by different electrons, until it is broken in two, is perhaps debatable. Whichever is the correct explanation in that case, a similar one in this case should probably be given. So that we would need to look on the arc as an instance where the normal anode drop has been diminished by the concentration of current.

Summary. — The anode drop was examined with the luminous discharge produced by hot CaO when pressures of the gas were low. It varies greatly as the distance between the anode and cathode is varied. It is greatest when they are near together and least when a few centimeters apart. As the distance between the electrodes is further varied, the anode appeared to move through the different parts of a striation and the anode drop depended on the part of the striation in which the anode is. The anode drop passes through a maximum value just before a new striation begins to appear. The same thing occurs when the striation is displaced by means of a magnet.

The anode drop varies greatly as the current through the tube is varied. It is large with very small and with very large currents. The amount of current corresponding to the minimum anode drop depends on the pressure of gas and the distance between the electrodes.

It is least when the anode is in the direct path of the cathode rays. It does not appear to depend on the electric force near the anode nor on the conductivity of the gas near the anode.

With pressures of the gas in the neighborhood of 1 mm. or more the anode drop is approximately independent of the current and of the distance between the electrodes and increases slightly as the pressure of the gas increases.

In hydrogen it is approximately the same as in air. It is the same for iron and mercury anodes, but an aluminum anode gives a higher value.

With currents in the neighborhood of .5 ampere there was a concentration of glow in one spot on the anode and with this a decrease in the anode drop. The discharge then appears to have all the characteristics of an arc.

The phenomena can be explained by assuming that at low pressures and with small currents the anode drop depended on the velocity of the negative ions at the anode, that with higher pressures it depended on the potential difference required to produce positive ions at the surface of the anode, and that with larger currents this ionization potential difference is modified by the concentration of current at one spot.

Part of the work described above was performed in the Cavendish Laboratory and I desire to express my thanks to Sir J. J. Thomson for allowing me the use of the laboratory and for his suggestions in regard to the work.

COLGATE UNIVERSITY,
June, 1909.

THE RESIDUAL OF INDUCTANCE AND CAPACITY IN RESISTANCE COILS. A STANDARD RESISTANCE WITH BALANCED INDUCTANCE AND CAPACITY.

By S. Leroy Brown.

I. Introduction.

A CAREFULLY constructed resistance coil can be standardized with direct current and its resistance accurately determined. The two principal errors attendant upon the use of such a coil with direct current are due to variations in its resistance caused by changes in temperature and thermo-electromotive force in the connections. The error caused by thermo-electromotive force can often be eliminated by reversing the current through the coil and the variations in temperature are reduced by making the coil of large wire, thereby reducing the heating effect of the current.

If a coil is used with interrupted or alternating current, two other errors must be guarded against. These are due to the inductance and the capacity of the coil. If no particular precaution has been taken to reduce both the inductance and the capacity to very small values, the coil may be entirely satisfactory when used with direct current but not at all satisfactory when used with alternating current. Some of the features in the design of resistance coils to be used with direct current are really disadvantages if the coils are used with alternating or interrupted current. For instance, making the coils of large wire and immersing them in oil or coating them with shellac, greatly increases their capacity. Without going further into the construction of resistance coils, it is clear that coils which are designed for direct current are not always adapted for use with alternating or interrupted current.

The wide application of interrupted and alternating current in measuring and comparing capacities and coefficients of induction necessitates, in many methods, the use of resistance coils which are measurably free from inductance and capacity. The inductance and

capacity of a resistance coil can be reduced to small values but neither can be reduced to zero. There will always be some magnetic area enclosed by the wires of the coil and some electrostatic capacity between the adjacent wires; but the capacity reduces the effective inductance. In well-constructed alternating-current coils the residual effect of inductance or capacity is made as small as possible. Since the effect of the capacity is equivalent to a negative inductance, the residual effect of inductance and capacity can be described as a positive or negative residual of inductance. The usual method of reducing this residual of inductance is to make both the inductance and capacity small, but apparently no attempt has been recorded to make the inductance exactly balance the capacity.

The double-wound resistance coil can be constructed nearly free from inductance, but the capacity of the wires is more difficult to eliminate. If the two wires of the coil enclose equal magnetic areas there remains only the small area between the wires to produce induction. The capacity depends upon the size of the wires and the closeness of winding. This capacity may be negligible in low-resistance coils, but for some purposes it may not be negligible in coils of higher resistance, especially if they are connected in parallel. By crowding together the two wires of the double-wound coil the inductance is reduced, but the capacity may be greatly increased.

Another method of constructing coils is to wind a single wire on a thin sheet of card-board or mica. The magnetic area per turn is reduced to the cross-sectional area of the sheet and the capacity may be made very small by separating the turns. Coils wound on this plan have a residual of inductance, depending upon the cross-sectional area of the material on which they are wound, since the capacity is reduced to a negligible quantity much smaller than the inductance.

Possibly the best method of winding coils is that devised by Chaperon,[1] and used in some of the resistance boxes manufactured by Hartmann and Braun. Several turns of a single wire are wound on a spool and then the direction of winding is reversed. The

[1] G. Chaperon, Comptes Rendus, 108, p. 799.

magnetic area enclosed after reversing the direction of winding is made equal to the area enclosed before reversing. Many sections, like the one described, make up the entire coil, which is then practically free from inductance. The coil is built in several divisions instead of having the layers carried the entire length of the spool. Beginning at one end, each division is completed before proceeding to the next adjacent division, so that the ends of the wire are at opposite ends of the spool when the coil is finished. Adjacent wires are therefore at a small difference of potential and the capacity is greatly reduced. In order to test any resistance coil for a residual of inductance or capacity a standard is required, free from inductance and capacity, or having one balanced by the other, or showing a known excess of one over the other. Coils could then be compared with the standard and described as having, for instance, 1,000 ohms resistance and 0.00001 henry residual inductance, or 1,000 ohms resistance and 0.001 microfarad residual capacity. Rosa and Grover,[1] of the Bureau of Standards at Washington, have called attention to the necessity of knowing the residuals of inductance of resistance coils when they are used with alternating current.

Such standards of comparison have been constructed already by reducing both the inductance and the capacity of the standards to values as small as possible. In this paper it is proposed to employ a different principle in the construction of the standard. Instead of seeking to make the inductance and capacity both small, it is proposed to offset one against the other, making the residual smaller than can be measured. If measurements of residuals less than a few hundred micromicrofarads are required, the latter plan offers noticeable advantages. In the standards hitherto constructed, the residuals are usually considerably greater than the amount indicated.

II. A Standard Resistance for Use with Interrupted Current.

Two long parallel wires, joined at one end, are to be separated to such a distance that the inductance and distributed capacity may balance. Suppose first a localized capacity, like a condenser,

[1] E. B. Rosa and F. W. Grover, Bulletin, Bureau of Standards, I., p. 291.

shunted by an inductive resistance. If a constant electromotive force be suddenly applied, current will flow as if the condenser were absent and the resistance non-inductive, provided that the so-called time-constant of the capacity C, shunted by the resistance R, equals the time-constant of the inductance L associated with the resistance R.

That is,

$$\frac{L}{R} = CR. \tag{1}$$

Stated more exactly, the defect in quantity passing through the inductive resistance during the period of variable flow, caused by the electromotive force of self-induction, is equal to the charge of the condenser, provided the time-constants are equal. In this sense the condenser-capacity balances the inductance.

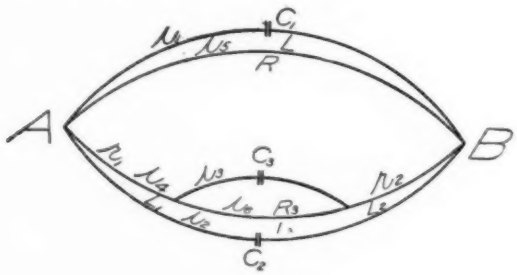

Fig. 1.

Suppose next, distributed capacity between the long parallel wires joined at one end. What is the time-constant of this arrangement? Consider the net-work of conductors shown in Fig. 1, divided into two systems, one consisting of the resistances r_1, r_2, R_3, capacities C_2, C_3 and inductances L_1, L_2, L_3, the other consisting of the resistance R, capacity C_1 and the inductance L. What is the condition that the one system may be equivalent to the other when a difference of potential is suddenly applied and maintained constant between A and B?

If the quantities of electricity q_1, q_2, etc., correspond to the currents i_1, i_2, etc., the equivalence of the two systems is expressed by

$$q_1 + q_5 = q_4 + q_2 = q, \tag{2}$$

where the integration covers the period of variable flow.

$$R_3 + r_1 + r_2 = R' + R_3 = R, \tag{3}$$

$$L_3 + L_1 + L_2 = L_3 + L' = L, \tag{4}$$

$$Ri_5 + L\frac{di_5}{dt} = R_3 i_6 + R' i_4 + L_3 \frac{di_6}{dt} + L' \frac{di_4}{dt}, \tag{5}$$

$$Rq_5 + LI_5 = R_3 q_6 + R' q_4 + (L_3 + L')I_5,$$

$$Rq_5 = R_3 q_6 + R' q_4. \tag{6}$$

From equation (2), expressing the quantities of electricity which flow into the condensers as the products of the capacities and the differences of potential at the terminals,

$$q_5 = q - q_1 = q - C_1 R I_5, \tag{7}$$

$$q_6 = q_4 - q_3 = q_4 - C_3 R_3 I_6 = q_4 - C_3 R_3 I_5, \tag{8}$$

$$q_4 = q - q_2 = q - C_2 R I_5. \tag{9}$$

I_5 and I_6 are the final values of the currents whose variable values are denoted by i_5 and i_6. Substituting these values of the quantities q_5, q_6 and q_4 in equation (6),

$$C_1 R^2 = C_2 R^2 + C_3 R_3^2. \tag{10}$$

This result can be extended by considering any number of condensers symmetrically distributed along a resistance which is equal to the resistance R, giving

$$C_1 R^2 = C_2 R^2 + C_3 R_3^2 + \cdots C_n R_n^2. \tag{11}$$

Therefore C_1 is a condenser, which if placed at the terminals of a resistance R, would be equivalent to the condensers C_2, C_3, etc., distributed along the resistance.

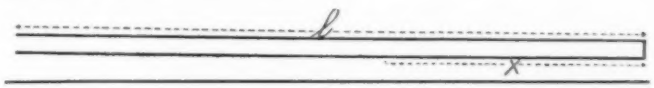

Fig. 2.

Let R be the resistance of two parallel wires which are connected at one end (Fig. 2). C_1 is the capacity per unit length of the parallel wires and C is a capacity, which, if placed at the terminals of the resistance R, would be equivalent to the distributed capacity.

The length of the double wire is l and x is the distance from the connected ends to any element of the parallel wires. The capacity

for an element of length of the wires is $C_1 dx$ and the resistance in parallel with this element of capacity is Rx/l. From equation (11)

$$CR^2 = \int_0^l \frac{C_1 R^2 x^2}{l^2}\, dx = \frac{C_1 R^2 l}{3} \qquad (12)$$

or $CR = C' \cdot R/3$ where C' is the entire capacity of the wires when they are not connected at either end. Therefore the effective capacity or the so-called time-constant of a capacity uniformly distributed as in Fig. 2 is one third as much as it would be if the entire capacity of the wires were located at the terminals of the resistance.

Let D be the distance between the wires and r their radius. Assume that the specific inductive capacity of the medium between the wires and the permeability of the medium, including the wires, are both unity. The inductance of the wires is given by the formula,

$$L = 4l\left(\log_e \frac{D}{r} + \frac{1}{4}\right) \text{ electromagnetic units}$$

and the capacity is given by the formula,

$$C' = \frac{l}{4 \log_e (D/r - 1)} \text{ electrostatic units.}$$

The equivalent capacity C is $C'/3$ and the effective capacity and inductance, expressed in practical units, are

$$C = \frac{l 10^{-11}}{9 \cdot 12 \cdot 2.3026 \log_{10}(D/r - 1)} \text{ farads} \qquad (13)$$

and

$$L = 4 \times 10^{-9} l \left[2.3026 \left(\log_{10} \frac{D}{r}\right) + \frac{1}{4}\right] \text{henrys,} \qquad (14)$$

the length l being measured in centimeters.

If an electromotive force is suddenly applied at the terminals of these parallel wires and maintained constant, the residual inductance will be zero when the inductance and capacity have equal time-constants. Substituting the values of C and L in the equation of the time-constants (equation (1)),

$$4\left(2.3026 \log_{10} \frac{D}{r} + \frac{1}{4}\right) 12 \cdot 2.3026 \log_{10}\left(\frac{D}{r} - 1\right) 9 \cdot 10^2 = R^2. \qquad (15)$$

The first attempt to satisfy the conditions expressed in equation (15) led to the construction of a parallel-wire standard having the following dimensions. Two number 35 german silver wires were placed 0.88 cm. apart; their common radius was 0.0067 cm.; and their length was 2,751 cm. This length yielded a resistance of 1,040 ohms as required by the substitution of the calculated inductance and capacity in equation (15).

Several resistance coils were compared with the standard by means of a Wheatstone network. The connections of a Leeds and Northrup moving-coil galvanometer and the battery were made through a secohmmeter. The bridge was balanced in the usual way before the secohmmeter was started. The deflection of the galvanometer, when the secohmmeter was rotating, was thus a measure of the residual inductance of the resistance coil which was being compared with the standard. In order that the residual inductances in the ratio-arms of the bridge might not produce a deflection of the galvanometer, they were selected so that when interchanged the balance was not disturbed. The galvanometer was calibrated by determining the capacity which must be added in parallel with the standard to produce 1 mm. deflection.

Measurements of resistance-coils used in the laboratory showed that in coils wound according to the Chaperon system, the effects of capacity and inductance were nearly balanced, but in coils wound in the ordinary bifilar fashion, the capacity over-balanced the inductance. That is, the double-wound coils would be described as having a negative residual of inductance. The residuals of inductance in the double-wound coils were balanced by capacities ranging from 0.0005 to 0.001 microfarad connected across the terminals of 1,040 ohms.

III. A Standard Resistance for Use with Alternating Current.

The next problem undertaken was the investigation of the conditions for balanced inductance and capacity when alternating current was used, instead of interrupted, steady current. The effect of inductance in general is to cause the current in a resistance to lag in phase behind the impressed electromotive force, while the effect of

capacity alone is to cause the current to precede the electromotive force in phase. There is neither lag nor advance when inductance is balanced by capacity.

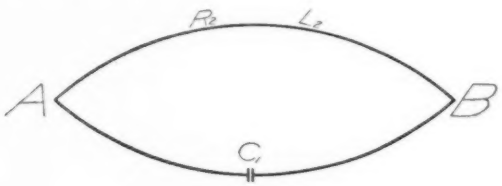

Fig. 3.

Fig. 3 represents an inductive resistance in parallel with a capacity. The circuit between A and B consists of two branches; the resistance, capacity and inductance of the branches are respectively $R_1 = 0$, C_1, $L_1 = 0$ and R_2, $C_2 = \infty$, L_2. Let an electromotive force which follows the simple harmonic law of variation with time ($e = E \sin \omega t$) be impressed between A and B, and consider the relations among C_1, R_2 and L_2 when the current flows in phase with the electromotive force.

Let the resistance, capacity and inductance of a single circuit which is equivalent to the two branches be R, C, L. Bedell and Crehore [1] have deduced the following equations between the resistances, capacities and inductances of parallel circuits and the resistance, capacity and inductance of a single circuit which is equivalent to the parallel circuits. The symbols without the subscripts refer to the equivalent, single circuit and the symbols with similar subscripts refer to the same branch of the parallel circuits.

$$\frac{1}{C\omega} - L\omega = \frac{B\omega}{A^2 + B^2\omega^2}, \tag{16}$$

$$A = \Sigma \frac{R_1}{R_1^2 + (1/C_1\omega - L_1\omega)^2}, \tag{17}$$

$$B\omega = \Sigma \frac{1/C_1\omega - L_1\omega}{R_1^2 + (1/C_1\omega - L_1\omega)^2}, \tag{18}$$

$\omega = 2\pi$ times the frequency.

Substituting the values of the resistances, capacities and induc-

[1] Bedell and Crehore, "Alternating Currents," 1895, p. 303.

tances given for the circuit of two branches (Fig. 3),

$$A = \frac{R_2}{R_2^2 + L_2^2\omega^2}, \tag{19}$$

$$B\omega = C_1\omega - \frac{L_2\omega}{R_2^2 + L_2^2\omega^2}, \tag{20}$$

$$\frac{1}{C\omega} - L\omega = \frac{C_1\omega(R_2^2 + L_2^2\omega^2) - L_2\omega}{1 + C_1^2\omega^2(R_2^2 + L_2^2\omega^2) - 2C_1L_2\omega^2}. \tag{21}$$

If a single circuit with a resistance R, a capacity C and an inductance L has impressed on it an electromotive force $e = E \sin \omega t$, the current is

$$i = \frac{E}{\sqrt{R^2 + (1/C\omega - L\omega)^2}} \sin\left[\omega t + \tan^{-1}\left(\frac{1}{CR\omega} - RL\omega\right)\right]. \tag{22}$$

Putting $1/C\omega = L\omega$; then $i = E/R \sin \omega t$ and the current and electromotive force are in phase. When $1/C\omega = L\omega$, the relation among R_2, C_1 and L_2 is determined by equation (21).

$$R_2^2 + L_2^2\omega^2 = L_2/C_1. \tag{23}$$

In a standard similar to the one described for interrupted current, the term $L_2^2\omega^2$ is negligible in comparison with the term R_2^2 for moderate frequencies and equation (23) becomes

$$R_2C_1 = L_2/R_2. \tag{24}$$

In order to secure a zero residual of inductance, the relation among the resistance, capacity and inductance is therefore approximately the same when either interrupted steady current or alternating current of moderate frequency is applied to a coil of small inductance.

The effective value of the uniformly distributed capacity of two parallel wires connected at one end was determined by experiments made with alternating current as described in Section V. of this paper. The results indicate that the effective capacity was one third of the total distributed capacity of the two parallel wires when disconnected at both ends. The standard proposed for interrupted current can therefore be used with alternating current of moderate frequency. When the parallel-wire standard is used with alternating current, the values of the capacity and inductance expressed in equation (24) are given by equations (13) and (14).

IV. DESCRIPTION OF A GALVANOMETER FOR ALTERNATING CURRENT.

The experimental work mentioned above required an instrument to indicate small differences of alternating potential. A disturbance in the bridge balance produced by only a few micromicrofarads of capacity added in parallel with the standard had to be detected in order to make accurate measurements, since the effective capacity of the 1,040-ohm resistance was only 52 micromicrofarads. That is, the distributed capacity, found by calculation from the dimensions of the wires was equivalent to no more than 52 micromicrofarads of capacity connected across the free ends of the wires in the form of a condenser. The instrument used for this purpose was an alternating-current galvanometer, similar to the one described and used by Stroud.[1] A disturbance in balance could be detected with this galvanometer when a capacity as small as 2 micromicrofarads was added in parallel with the 1,040 ohms.

This galvanometer, as described by Stroud, is similar to an ordinary moving-coil galvanometer, but it has a wire-wound field-magnet with laminated, soft iron poles and yoke instead of a permanent magnet. The poles and yoke were built of U-shaped stampings of soft iron insulated from each other by a thin coat of shellac. The dimensions of these stampings were 12.8 cm. by 25.4 cm. by 0.039 cm. with a gap 3.85 cm. by 16.6 cm. These stampings were piled 3.85 cm. thick and cemented together with shellac. Each leg of the U was wound with 625 turns of number 22 insulated copper wire forming a coil 12.8 cm. long. The armature was a rectangular coil 3.85 cm. by 3.12 cm. by 0.78 cm. wound with 1,500 turns of number 40 silk-covered, copper wire. It was suspended between the upper faces of the U-shaped field magnet by a number 40 phosphor-bronze wire 30 cm. long. Connection to the armature was made above through the suspension and below by a wire dipping into mercury.

The galvanometer is not sensitive to differences of potential which are in phase with the electromotive force which excites the field magnet, but it is extremely sensitive to differences of potential which are in quadrature with the exciting electromotive force. When the same electromotive force which excites the field magnet

[1] W. Stroud, Phil. Mag., Vol. 6, 1903, p. 707.

is applied to a Wheatstone bridge, the galvanometer is very sensitive to differences of potential due to capacities or inductances in the arms of the bridge. The resistances of the bridge were balanced by using direct current and a moving-coil galvanometer, and then, without changing the resistances, the capacities and inductances were balanced by using alternating current and the alternating-current galvanometer. Leakage in the condensers or lack of accurate balance among the resistances does not appreciably affect the balance between the capacities and inductances. The alternating-current galvanometer is not sensitive to differences of potential due to small leakage currents or a slight inaccuracy of balance among the resistances, since the differences of potential are in phase with the applied electromotive force.

V. Connections and Measurements.

The connections of the galvanometers and sources of electromotive force to the bridge are shown in Fig. 4.

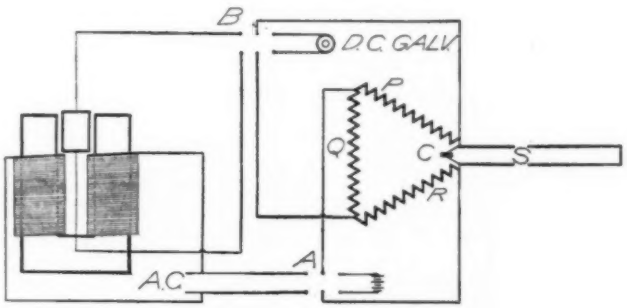

Fig. 4.

Switches A and B are thrown to the right and the bridge is accurately balanced with direct current. Then switch B is thrown to the left and the equilibrium position of the moving coil of the alternating-current galvanometer is noted with telescope and scale. Switch A is then thrown to the left and the deflection noted if there is lack of balance between the capacities and inductances of the bridge. The ratio arms P and Q are selected so that when they are interchanged, the balance is not affected. If R has a greater negative residual of inductance than S, a balance can be obtained by

adding a small known capacity at C. If R has a greater positive residual of inductance than S, the capacity is added in parallel with R instead of S. C is a variable capacity made of tin-foil on plates of glass with a range from 2 to 7,000 micrimicrofarads. The source of electromotive force was an inverted rotary converter, driven by a storage battery. The rotary converter produced a constant electromotive force and prevented any deflection of the galvanometer due to changes in its field. The frequency of the alternating current was 40 cycles per second.

The following experimental determinations were made with this apparatus. Pairs of parallel wires, placed at different distances apart, some less and some greater than the distance calculated for balance of inductance and capacity, were compared with the standard resistance. The pairs of wires had equal resistances so that the same resistance-coil in the arm R could be used with each pair. This avoided any error which might be introduced by inserting successively

TABLE I.

Resistance (Ohms).	Dist. Apart (cm.).	Calc. L (mil. h.).	Calc. C (cm.).	C (mmf.) Necessary to Add	
				By Cal.	By Exp.
1,037.2	.88	.056	52	0	0
1,037.2	.335	.046	65	−22	−20
1,037.2	1.35	.061	48	8.5	10
1,037.2	6.67	.082	38	40	35

coils having different residuals of inductance when balancing R against successive pairs of wires. The ratio-arms were chosen so that the balance was not disturbed by interchanging them. The standard was first placed in the arm of the bridge denoted by S in Fig. 4 and capacity added at C until a balance was obtained. The standard was then replaced by another pair of parallel wires and C changed until a balance was again obtained.

The calculations were made on the assumption that the effective capacity was one third of the total capacity of the two wires when not connected at either end. The results expressed in Table I. show a close agreement between theoretical and experimental values.

The effective value of a uniformly distributed capacity was also

determined experimentally by measuring the effect of 2,500 micro-microfarads capacity when connected successively at different points along the parallel wires. The deflections of the galvanometer were first taken as a measure of the effect of the 2,500 micromicrofarads capacity. Suspecting that the calibration curve of the alternating-current galvanometer might not be a straight line, the amount of capacity required in parallel with the arm R to bring the armature of the galvanometer to its equilibrium position was taken as the measure of the effect of the capacity connected at different points along S.

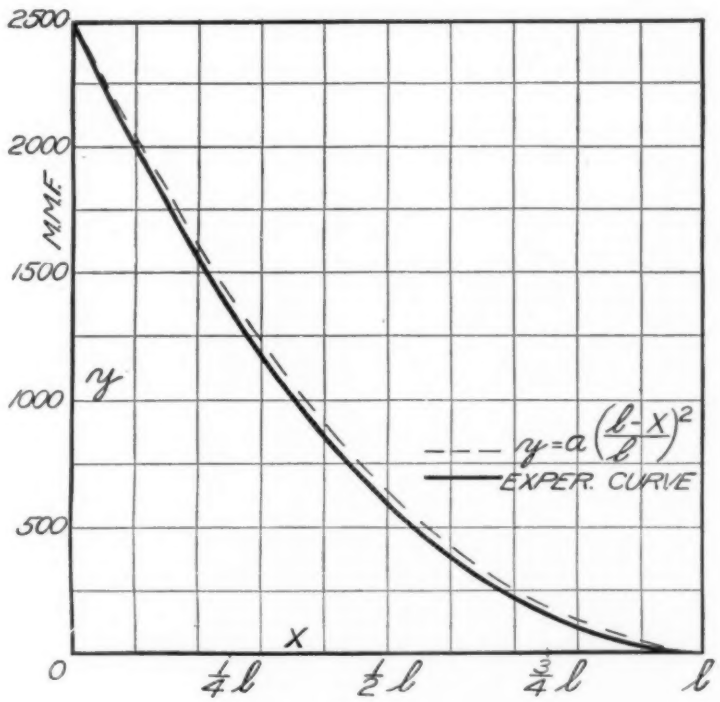

Fig. 5.

A curve was then plotted with abscissas representing the distances of the connections of the capacity from the terminals of S and ordinates representing the capacities required in parallel with R to balance the capacity in S.

Fig. 5 shows the close agreement between this curve, obtained

experimentally, and the curve $y = a(l - x)^2/l^2$, wherein l is the length of the parallel wires and a is the greatest ordinate of the curve plotted from experimental data. The measure of the effect of the capacity connected at different points along S decreases with the square of the fractional part of the total resistance, which shunts the capacity. Therefore, as shown by the agreement between the equation of this curve and the expression employed in equation (12), the integrated effect of a uniformly distributed capacity would be one third of the effect of the same capacity located at the terminals.

VI. The Residuals of Inductance in Ordinary Resistance Coils.

A balanced standard consisting of two parallel wires was next used to determine the residuals of inductance of resistance-coils from different makers. For convenience of comparison a new standard was constructed of number 35 german silver wires, placed 0.77 cm. apart and having a resistance of 1,000 ohms. A sliding contact-piece at the connected ends of the wires provided for small adjustments of resistance.

Referring again to the scheme of connections shown in Fig. 4, S is now the 1,000-ohm standard and R is the resistance-coil or series of connected coils under test. Table II. shows the results of the measurements. Positive values of C indicate that capacity predominates in the resistance R; negative values indicate that the capacity was inserted in parallel with R instead of S, that is, that inductance predominates in R. The values of C were determined within about 25 micromicrofarads. When the resistance of arm R was 2,000 ohms, two 1,000-ohm standards were used in arm S.

VII. A Standard of Variable Resistance Apparently Impracticable.

An increase in the resistance of a standard requires a new adjustment between the capacity and the inductance if they are to remain balanced. According to equation (24), the inductance must increase faster than the capacity if balance is maintained when the resistance increases. If a variable resistance standard is constructed similar

TABLE II.

Description of Coils.	Number of Resistance Box.	Resistance (Ohms).	Residual Capacity (mmf.).
Hartmann and Braun "double-wound" coil.	3,213	1,000	1,120
	3,215	1,000	1,110
	3,213 in series	1,000	
	with 3,215	1,000	585
	4,549	400+300+200+100	1,245
	3,995	400+300+200+100	730
	2,313	2,000	2,275
	3,215	2,000	2,130
	3,995 in series	400+300+200+100	
	with 4,549	400+300+200+100	450
Hartmann and Braun "Chaperon-wound" coil.	3,028	1,000	105
	3,028	400+300+200+100	−260
	3,028	2,000	60
Wolff "double-wound" coil.	3,187	1,000	735
	3,187	1,000	760
	3,187	2,000	1,140
	3,187 in series	1,000	
	with 3,187	1,000	390
Leeds and Northrup "double-wound" coil.	4,491	1,000	610
	4,492	1,000	630
	4,491 in series	1,000	
	with 4,492	1,000	330
	4,492	2,000	835
	4,491	2,000	860
	4,491 in parallel	2,000	
	with 4,492	2,000	1,875

to the 1,040- and 1,000-ohm standards already described, the distance between the wires must increase with the distance from the terminals. Increasing the resistance by connecting the wires together farther from the terminals, would then increase the inductance faster than the capacity. The impracticability of such a construction is easily seen from a single example.

Beginning with 500 ohms of number 35 wire the uniform distance between the wires, as determined by equation (15) would be 0.0635 cm. If 100 ohms are added, the uniform distance between the wires in the added section, in order that the 600 ohms may be free from residual of inductance or capacity, is determined as follows.

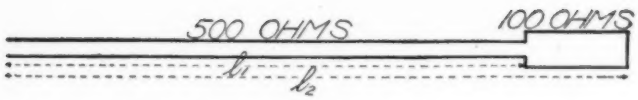

Fig. 6.

Let C_1 and C_2 be the capacity per unit length for the 500-ohm and 100-ohm sections respectively. According to equation (12) the effective capacity C of the two sections is

$$C = \int_0^{l_2-l_1} \frac{C_2 x^2 dx}{l_2^2} + \int_{l_2-l_1}^{l_2} \frac{C_1 x^2 dx}{l_2^2}, \qquad (25)$$

$$l_1 = \tfrac{5}{6} l_2.$$

Equations (12) and (15) were derived on the assumption that the standard was to be used with interrupted current but experimental results have shown that the same equations apply when alternating current is used. The total inductance is the sum of the inductances of the two sections.

$$L = L_1 + L_2.$$

The effective capacity of the 500-ohm section is increased about one fifth by adding the 100 ohms, but the effective capacity of the added section is small, since no part of it is shunted by much resistance and the wires are far apart in order to increase the inductance sufficiently. The relative contribution of the two sections can be determined from equation (25). Therefore the effective capacity is increased approximately one fifth and the square of the resistance is increased about one half by adding the second section. Then, according to equation (24), the total inductance must be increased to about one and four fifths times the inductance of the 500-ohm section and this would require that the wires in the 100-ohm section should be 106 cm. apart.

This emphasizes the necessity of a comparatively high inductance in a double-wound high resistance-coil if the last few turns are close together. Ordinarily the two wires of the double-wound coils are wound side by side throughout the entire coil and therefore the inductance is not sufficient to balance the capacity in coils of higher resistance.

VIII. The Residual Inductance of a Coil Made by Twisting the Wires Together and Separating Consecutive Terms.

A so-called "ideal coil" has been constructed by Taylor and Williams,[1] whose purpose was to make both inductance and capacity as small as possible. With their coil, having braided bifilar windings, the consecutive turns being separated 5 mm., they detected no residual capacity, even with a very sensitive alternating-current galvanometer, though the capacity had been increased by immersing the coil in petroleum. Since the inductance had been made very small by twisting the wires together, it was concluded that both the inductance and the capacity had been effectively reduced below measurable quantities.

From results obtained with the apparatus described in the present paper, it appeared that a twisted-wire standard is not sufficiently free from capacity if residuals of only a few micromicrofarads are to be detected and measured. A coil similar to that of Taylor and Williams was constructed and the excess of capacity over inductance was determined both by calculation and experiment.

The coil constructed by the writer was made of two number 35 double silk-covered german silver wires, soldered together at one end. The wires were twisted together and wound on a rectangular block 11 cm. by 12 cm. in section. The length of the bifilar winding was 2,750 cm., the wires having a resistance of 1,000 ohms. The distance between consecutive turns was about 0.4 cm. By the aid of a microscope, the distance between the centers of the wires was determined to be 0.021 cm. In some places, however, where the pressure between the wires was sufficient to deform the covering, the distance between the centers of the wire was probably slightly less.

Comparisons of this rectangular coil with the parallel wire standard showed a considerable excess of capacity over inductance in the former. When the coil was in air, 420 micromicrofarads of capacity were added in parallel with the standard to obtain a balance. The coil was immersed in petroleum and 685 micromicrofarads of capacity were required in parallel with the standard to effect a balance. After removing the coil from the petroleum bath,

[1] A. H. Taylor and E. H. Williams, Phys. Rev., XXVI., p. 417, 1908.

but with the covering on the wires still moistened with oil, the capacity measured 585 micromicrofarads. This value is between the values obtained when the coil was in air and when it was in oil.

Assuming unit specific inductive capacity of the dielectric between the wires and that the distance between the centers is 0.021 cm., the excess of capacity is 355 micromicrofarads by calculation. If petroleum is assumed as the dielectric the excess of capacity is about 800 micromicrofarads. This value is to be compared with the value 685 micromicrofarads obtained experimentally. The discrepancy between calculated and experimental values may be accounted for by remembering that the dielectric was not entirely petroleum in one case nor air in the other.

Comparing these results with the negative results obtained by Taylor and Williams, it should be noted that they used number 40 advance wire, while the coil here described was constructed of number 35 german silver wire. If it had been made of number 40 german silver wire, having the same resistance, 1,000 ohms, and the same distance between the twisted wires, the residual capacity would have been, by calculation, only 155 micromicrofarads.

The capacities of the 1,000- and 2,000-ohm coils of resistance box number 3,187, made by Otto Wolff of Berlin, were measured by comparison with the parallel-wire standard. The coils are made of rather large wire, wound on brass cores and heavily coated with shellac. The 1,000-ohm coil showed 750 micromicrofarads of capacity and the 2,000-ohm coil about 1,140 micromicrofarads. These values are seen to be higher than those found by Taylor and Williams.

IX. Balanced Inductance and Capacity Using Wire with Permeability Greater than Unity.

In the calculation of the inductance of the parallel wire standard, the permeability of the wire was assumed to be unity. If the wires are made of a metal having a permeability greater than unity, the inductance would be greater than that already calculated. In most resistance coils of 100 ohms or more, wound in the ordinary bifilar method, there is a residual of capacity. If then, wire of sufficiently high permeability could be found, it seems to be theoretically possi-

ble to balance inductance against capacity, without separating the wires as has been done in the case of the parallel-wire standard described in this paper. The self-inductance of a return circuit consisting of two parallel iron wires, l cm. in length, r cm. in radius, D cm. apart, joined at one end, is

$$L = 4l\left(2.3026 \log_{10}\frac{D}{r} + \frac{\mu}{4} - \frac{D}{l}\right),^{1}$$

wherein μ is the permeability of the wires, that of the medium between the wires being unity. Applying this formula to the calculation of the residual of inductance in the 1,000-ohm coil, made by twisting the two wires together and separating consecutive turns, a value of μ less than 40 is found to be sufficient to make the inductance balance the capacity when the medium between the wires is air.

The magnitude of the increase of the inductance due to the permeability of the wire in the coil was experimentally investigated by comparing a coil of iron and a coil of superior wire with coils of german silver wire. The iron-wire coil was made by winding two number 32 wires, 0.15 cm. apart, on a cylindrical, wooden frame 25 cm. in diameter. The two wires were soldered together at one end and consecutive turns were separated about 1 cm. The length of the wire in the bifilar coil was about 274 meters, having a resistance of 1,000 ohms. The superior wire coil was made by winding two number 26 wires, 0.1 cm. apart, on a rectangular wooden block 9.25 cm. square. The length of the wire in this bifilar coil was 40 meters, having a resistance of 265 ohms.

These coils were compared with similar coils of german silver wire placed in one arm of the Wheatstone bridge and balanced against the parallel-wire standard according to the method described above (Section V. and Fig. 4). The german silver coil was then replaced by a coil of iron or of superior wire and balance again obtained. In no case was the increase of inductance due to the permeability of the wires sufficiently large to be measured.

[1] E. B. Rosa and L. Cohen, Bulletin Bureau of Standards, V., p. 51, 1908.

X. MEASUREMENTS WITH ALTERNATING CURRENT AT FREQUENCIES RANGING FROM 420 TO 700 CYCLES PER SECOND.

All the measurements described heretofore were made with interrupted steady current or with alternating current at a frequency not exceeding 40 cycles per second. Higher frequencies were next used to determine to what extent the values of the residuals depend upon the frequency of the applied electromotive force. The source of electromotive force used first was a small eight-pole generator with an armature which could be rotated at speeds as high as 3,600 R.P.M. The residuals of inductance of several resistance coils were measured with this source of electromotive force at 240 cycles per second. The differences between these values and those obtained with alternating current at 40 cycles per second were within the limits of experimental error.

In order to test further the effect of higher frequencies a small twenty-pole generator with a Gramme ring armature was used as a source of electromotive force. This generator was capable of producing alternating current at frequencies ranging from 500 to 800 cycles per second but it gave a voltage insufficient to excite the field magnet of the galvanometer. A small galvanometer was then built with all of the dimensions reduced to about one fifth of those of the galvanometer described in Section IV. The results of the measurements made with this galvanometer and the twenty-pole generator did not agree with those made with alternating current at 40 cycles per second. However, the same results were obtained when the frequency was 700 cycles per second as when it was 500 cycles per second. The measured residuals of capacity of 1,000-ohm double-wound resistance-coils, obtained at either frequency with the twenty-pole generator as a source of current, were 10 or 12 per cent. higher than those obtained with alternating current at 40 cycles per second. Investigaton showed that the cause of these discrepancies was a small direct electromotive force which was superimposed upon the alternating electromotive force. When the direct electromotive force was balanced by a battery, the differences vanished and the results obtained at 40 cycles per second were repeated with current at the higher frequency.

The measurements at higher frequencies could not be made as

accurately as those at 40 cycles per second. The probable error of the observations in measuring capacities of 1,000 micromicrofarads was at least 5 per cent. The results of the experiments with higher frequencies can therefore be stated as follows: With frequencies ranging from 240 to 700 cycles per second, the same values of residuals of inductance are obtained and if there is a correction depending upon the frequency, it is certainly less than 5 per cent. for this range. The values of the inductance and capacity of the coils tested were both small, never exceeding a few microhenrys or a few hundred micromicrofarads. That the balance of inductance and capacity of a resistance coil is independent of the frequency for low frequencies and small values of inductance is to be expected from equation (23). The term $L^2\omega^2$ is too small to produce a measurable effect when resistance coils of small inductance are measured.

XI. Measurements of Larger Values of Inductance.

When the inductance of a coil is not small, the term $L^2\omega^2$ may not be negligible in comparison with R^2. The relation among the resistance, capacity and inductance, when the current flows through the coil in phase with the electromotive force, is given by equation (23) instead of equation (24).

The validity of equation (23) was tested experimentally by applying it to coils of larger inductance. Coils having an inductance of a few hundred millihenrys were inserted in one arm of the Wheatstone network (R of Fig. 4) and a capacity in parallel with R was adjusted until it balanced the inductance. The experimental manipulation was the same as when the bridge was balanced with coils of small inductance. The capacities used were those of standard mica condensers. The inductance of the coil is found from equation (23), substituting $\omega = 2\pi n$, n being the frequency of the applied electromotive force.

An inductance coil of about 0.1340 henry was measured by this method with currents at frequencies ranging from 62 to 700 cycles per second. The values of the inductance calculated from equation (23) for this range of frequencies did not differ more than 16 parts in 1,340. A standard inductance of 0.1 henry made by Hartmann and Braun was measured with the same range of frequencies and

the values did not differ from 0.1 henry more than one half of one per cent. The same method is also applicable to the measurement of capacity by comparison with standard inductance.

Below is a table showing the results of measurements of two standards of inductance made by Hartmann and Braun and inductance coil number 7 taken from the laboratory.

TABLE III.

R (Ohms).	L (Henrys).	C (mf.).	Freq. Cycles Sec.	Cal. L (Henrys).
1,000	0.1	0.0996	62	0.0996
1,000	0.1	0.0965	300	0.1000
1,000	0.1	0.0905	500	0.0994
1,000	0.1	0.08325	700	0.0995
1,000	0.2	0.197	62	0.1985
1,000	0.2	0.143	500	0.1996
1,000	0.2	0.110	700	0.1952
1,000	Coil No. 7	0.1333	62	0.1338
1,000	Coil No. 7	0.125	300	0.1332
1,000	Coil No. 7	0.124	333	0.1340
1,000	Coil No. 7	0.0995	700	0.1341
1.000	Coil No. 7	0.1000	700	0.1348

This application of the alternating-current galvanometer affords an excellent method for measuring capacities and inductances, applicable to both small and large values of inductance or capacity; and the calculations involve only simple formulæ. After the galvanometer is put into good adjustment, measurements can be made quickly and accurately; but the chief advantage of the method is that the quantities entering the calculations are only the resistance, inductance and capacity of the arm of the bridge and the frequency of the applied electromotive force.

CONCLUSIONS.

1. A parallel wire standard of resistance can be constructed which is free from residual inductance when used with interrupted, steady current or with alternating current of moderate frequency.

2. The outstanding difference between inductance and capacity in resistance coils can be measured by comparison with this parallel-wire standard.

3. A standard coil, made by twisting the wires together and

separating consecutive turns is not completely compensated for inductance and capacity when capacities of a few hundred micro-microfarads are to measured.

4. Capacities and inductances of small or large values can be measured with alternating current and an alternating-current galvanometer. The values are calculated from formulæ which involve only the resistance, inductance and capacity of a single circuit and the frequency of the applied electromotive force.

UNIVERSITY OF CALIFORNIA,
April 15, 1909.

A STUDY OF THE REFLECTING POWER OF METALS AS DEPENDENT ON THE REFRACTVIE INDEX OF THE SURROUNDING MEDIUM.

BY L. R. INGERSOLL AND R. T. BIRGE.

INTRODUCTION.

THE object of this paper is an experimental study of the reflecting power of metals in media (*i. e.*, *liquids*) of various optical densities.

As is well known, the Fresnel reflection laws for surfaces of transparent substances apply equally well to such surfaces when overlaid or surrounded with a liquid (say) if the index of refraction of the substance is taken as relative to that of the liquid. In metals we have a more complicated case, for the formula for reflecting power at normal incidence as stated by Drude [1]

$$R = \frac{n^2(1 + k^2) + 1 - 2n}{n^2(1 + k^2) + 1 + 2n}$$

involves two constants, n the refractive index and k the absorption index of the metal. For the case of a metallic surface in contact with a transparent medium of index other than unity, the above formula is customarily extended by the assumption that the refractive index is then to be taken as relative to that of the medium, the absorption index remaining practically constant. From a somewhat different standpoint Maclaurin [2] arrives at similar conclusions.

While the above assumptions are quite reasonable, this formula as applied to metal surfaces overlaid with transparent substances has never been subjected to experimental proof. The few scattering observations which are recorded, such as that of Hagen and Rubens [3] on the reflection of glass backed by silver, and of Conroy [4] for a

[1] Lehrbuch der Optik, 1906.

[2] R. C. Maclaurin, Theory of Light, Part I., Camb., 1908, pp. 249 and 261 .

[3] Hagen and Rubens, Ann. d. Phys., I., p. 352, 1900.

[4] J. Conroy, Proc. Roy. Soc., 35, p. 26, 1883; 28, p. 242, 1879; 31, p. 486, 1881.

particular case of steel under water, are not in sufficiently good agreement with the theory to give it any support.

On the other hand Conroy, Des Coudres,[1] and a number of other investigators[2] have studied the related problem of the influence of an overlying medium on the measured optical constants of a metal. The results[3] in the case of Conroy have been discussed by Voigt[4] and Drude[5] and are in fair agreement with the theory, but somewhat low. The presence of a transition layer has been assumed to explain the remaining discrepancy, but the two additional constants[6] which are introduced to take account of a transition layer, and which are determined from the results themselves, necessarily bring about a better apparent agreement between theory and facts; hence this assumption is to be avoided if possible.

In the present work an attempt is made to show that the reflecting power of perfect metal surfaces in various liquids is in good agreement with the simple theory outlined above. Surfaces imperfect because of scratches and other defects have also been studied, and while they do not by any means afford results identical with those of perfect surfaces, an empirical law is deduced which expresses the relation between their reflecting powers in air and in another medium.

Method and Apparatus.

The method of measuring reflecting power was that of comparison with a known standard, *e. g.*, a silver surface. For this purpose a spectrophotometer of the Martens-Koenig type was used and the optical train arranged as in Fig. 1. One half the field of view in the spectrophotometer was illuminated by light from the Nernst glower G, reflected from the concave mirror M_1 and the small prism: the other half by light reflected in succession at M_2; at S, which was either the comparison mirror or the surface to be tested, each

[1] Des Coudres, Inaugural Dissertation, Berlin, 1887.

[2] G. Quincke, Pogg. Ann., 128, p. 541, 1866. Also P. Drude, Wied. Ann., 39, p. 481, 1890.

[3] The angle of principal incidence was decreased on surrounding a metallic surface with a liquid. The principal azimuth was only slightly affected, if at all; in some cases it showed a very small increase.

[4] W. Voigt, Wied. Ann., 23, p. 137, 1884.

[5] P. Drude, Wied. Ann., 39, p. 481, 1890.

[6] R. C. Maclaurin, Theory of Light, p. 251.

being in the form of a small plane mirror ; at M_3 ; and from D into the instrument.

The focal lengths of the mirrors (between 30 and 40 cm.) were so chosen that sharp images of the glower were formed on each slit of the spectrophotometer, as well as on the surface S. The advantage of working with the surface to be tested in the focus of the beam are obvious, when it is considered that in this way a minimum of surface is required, and moreover any small departure of the surface from planeness is of least effect under such circumstances. The departure from strictly normal incidence — about 5° — was not enough to affect the reflecting power to an appreciable extent.

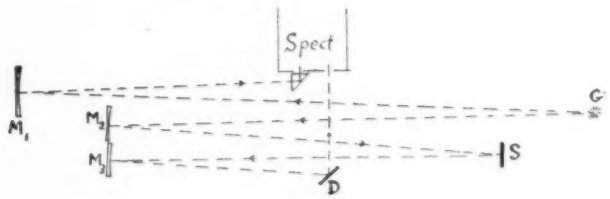

Fig. 1.

Comparison Mirrors. — For such, a large number of plate glass surfaces were silvered by the Brashear process and polished with rouge and chamois skin. Of perhaps twenty which were tested, the reflecting power of the best was, for a variety of reasons, assumed at 94.5 per cent., for the wave-length of sodium light, this being the wave-length used exclusively in this investigation. The average reflecting power of the surfaces tested was, on the assumption of the best being 94.5 per cent., about 93 per cent., which was that found by Hagen and Rubens [1] for a surface of much larger area than these. The theoretical reflecting power of silver computed from its optical constants is somewhat larger than either of these values, viz., 95.1 per cent. for sodium light.

But while the probable error of this assumption of reflecting power is not thought to exceed one half per cent., such a surface would be very difficult to use as a working standard, as it would be subject to continual change ; hence it was immediately compared with three other surfaces, viz., a plate of polished steel, one of pol-

[1] Ann. d. Phys., I., p. 352, 1900 ; 8, p. 1, 1902.

ished silicon, and an iron cathode surface. The last two apparently suffered no loss of reflecting power with age, while the steel surface changed only slightly and was frequently compared with the other two to eliminate any error from this source.

Observations. — In any series of observations a considerable number of settings of the spectrophotometer were first made with the comparison mirror in the position S. The surface to be tested was then introduced and a like number of settings taken, from which the relative reflecting power of the surface could be readily computed. The absolute reflecting power would, of course, follow on multiplication by that of the comparison mirror.

In measuring the reflecting power under liquids, small drops were placed on the surface and it was then covered with a slip of microscope cover glass of tested planeness, which spread the fluid out in a thin layer. To facilitate this part of the work it was found desirable to have the surface under test held horizontally. This was the arrangement used in the latter part of the work and was accomplished with the aid of an additional plane mirror (not shown in the diagram).

Correction. — The presence of the cover glass necessitated a small correction which was obtained as follows:

Let I be the intensity of the incident light, and I' the observed intensity of the reflected light. Let r be the fraction of light directly reflected at the air-glass and glass-liquid surfaces, the latter part being almost negligible. Then if R' is the fraction reflected at the liquid-metal surface, or in other words the reflecting power we desire to measure, we may write

$$I' = Ir + I(1-r)^2R' + I(1-r)^2R'\,r + \cdots.$$

The third term is so small that its value, Ic, may be computed with sufficient accuracy by assigning an approximate value to R'. Then

$$R' = \frac{(I'/I - r - c)}{(1-r)^2},$$

where r is approximately .040.

This gives at once the desired reflecting power R' from the measured apparent reflecting power I'/I.

Errors. — As a considerable number of settings of the spectrophotometer — usually twenty — were made for each measurement of reflecting power, the probable error arising from this source did not exceed one half per cent.

Inaccuracy of adjustment might easily cause an error several times as large as this and had to be carefully guarded against. A fruitful source of trouble of this sort was a tendency of the small cover slip to assume a tilted position when used with viscous liquids.

Contamination of the cover glass or surface under test might introduce considerable error. Great care was used in cleaning all surfaces with alcohol but in some cases a variation of the results is supposed to be due to this cause. Contamination of the comparison mirror or a wrong assumption as to its reflecting power would introduce errors in the determinations of the absolute reflecting powers, but would not affect our determination of the relative change of reflecting power when under the fluid, and, as will be noted later, this is of greater interest than the absolute reflecting powers.

Probable Error. — The general effect of the above sources of error is not enough, in our estimation, to cause a probable error in the determination of reflecting power in excess of one per cent. This is about the magnitude of the casual variations which are noted in the results.

RESULTS.

Metals. — The metal surfaces experimented upon were the following:

1. Silver on glass deposited chemically. Also glass-backed-by-silver mirrors on microscope cover glass.

2. A very perfectly polished steel mirror, as well as several steel surfaces ground with No. 0000 emery paper but not polished.

3. Several good silicon surfaces.

4. A rather imperfect gold surface obtained by buffing with rouge and machine oil.

5. Two cobalt surfaces gound with No. 0000 emery paper and polished with dry rouge.

6. Several cathode surfaces of platinum and iron.

With the exception of gold all the above surfaces were prepared

in this laboratory. The process in the case of steel consisted in rough grinding with graded emery or carborundum on an iron plate; then fine grinding with the finest precipitated powders on a lead disk, after which it was polished in the usual way with rouge and water, using a pitch and beeswax tool. Silicon was prepared in much the same way.

Liquids. — For determining the reflecting power in media other than air, the liquids monobromnaphtalin, Canada balsam, glycerine and water were tried. It was soon found, however, that satisfactory results could not be obtained with water or Canada balsam, as the former evaporated too quickly and the latter was too viscous. The results recorded are for glycerine ($N_D = 1.466$) and monobromnaphtalin ($N_D = 1.658$).

No attempt will be made at a detailed presentation of the results which embody in all several thousand observations, but the general conclusions may be readily drawn from the table and curves which follow. It will be convenient to consider the results under two general heads, viz., those for perfect and for imperfect surfaces, the word "perfect" applying to the state of polish, rather than of planeness.

Perfect Surfaces. — As practically perfect surfaces were considered those free from casual defects and which gave reflecting powers within one or two per cent. of the theoretical, computed from the optical constants of the metal. As may be realized, such surfaces are extremely hard to prepare and only three of those used in the present investigation — silver, steel and silicon — were of this class. Fortunately, however, these metals may be regarded as typical, since they represent, as regards their optical properties, the two extremes and the mean. Thus silver has a low index of refraction, high absorption, and high reflecting power, while silicon has a high index, low absorption and low reflecting power. The optical properties of steel are more nearly like those of the majority of metals.

In Table I. the results are given for these metals. The optical constants used for steel and silver are those of Drude. For silicon they had not been previously determined and were measured by Mr. J. T. Littleton, Jr., of this laboratory, to whom acknowledgment is also due for the preparation of the silicon surfaces. The figures are all for the wave-length of sodium light, $\lambda = 5893$ Å.U

TABLE I.

Metal.	Medium.	R		$\frac{R \text{ (liquid)}}{R \text{ (air)}}$		$\frac{1-R \text{ (liq.)}}{1-R \text{ (air)}}$	
		Theor.	Obs.	Theor.	Obs.	Theor.	Obs.
Silver $n = 0.18$	air	.951	.941				
$k = 20.39$	monobrom	.929	.912	.976	.969	1.462	1.490
	air	.951	.926				
	glycerine	.934	.892	.981	.964	1.360	1.458
	glass$_{(N_D=1.49)}$	.933	.912	.980	.978		
Steel $n = 2.41$	air	.585	.570				
$k = 1.41$	monobrom	.432	.416	.738	.730	1.368	1.358
	air	.585	.566				
	glycerine	.468	.444	.800	.785	1.281	1.280
Silicon $n = 4.10$	air	.385	.377				
$k = 0.20$	monobrom	.195	.187	.507	.497	1.310	1.305
	air	.385	.381				
	glycerine	.240	.232	.624	.609	1.235	1.240

The results for a glass-silver surface, included in the table, are of interest, as they show a somewhat better agreement with theory than those of Hagen and Rubens[1] for a similar case, in which they found a reflecting power of only 82–88 per cent. It is quite probable that the better agreement of the present results with theory is due to the very small area of surface used (about 1 mm. × 4 mm.), thus enabling one to select a very perfect part of the surface of such small area.

Conclusion for Perfect Surfaces. — An inspection of the above table shows that the experimental and theoretical results agree within what are probably the limits of experimental error. It is true that the observed values of R(liquid)/R(air) are uniformly a trifle low, and this might be explained by assuming a transition layer; but on the other hand, the small outstanding discrepancy could be readily accounted for by the fact that the mirrors tested only approximated perfect surfaces, as will be noted by the difference between the theoretical and observed values of R in air. In the ratio $[1 - R(\text{liquid})]/[1 - R(\text{air})]$, the particular significance of which will be discussed later, the disagreement is large in the case of silver; but it will be noted that this is the ratio of two very

[1] Ann. d. Phys., 1, p. 352, 1900.

small values and would be largely affected by a small experimental error.

We may then conclude for perfect metallic surfaces that the simple extension of the theory which is customarily made is experimentally justified. That is, the reflecting power when overlaid with a transparent substance of refractive index m, may be obtained by replacing in the formula for metallic reflection the index n of the metal by n/m, k remaining unchanged.

Imperfectly Polished Surfaces. — Because of the extreme difficulty, if not impossibility, of obtaining metallic surfaces with perfect polish, it becomes of interest to study these relations of optical properties under different media, for the case of imperfect surfaces. General planeness being assumed, the several causes for the departure of a surface from its "normal state," that is, a state of perfect polish, may be grouped under three heads:

(*a*) Opaque absorbing spots or masses covering some fraction of the area of the surface.

(*b*) A transparent surface layer of variable or constant index of refraction.

(*c*) Surface indentations or irregularities. This includes all such casual defects as corrugations, scratches, and "pit marks," of any size whatever.

The last class of defects is much the most common of the three, as the first two may be guarded against to a great extent by a suitable choice of abrasives for the final polishing and care in cleaning. To study briefly their effects on the reflecting power under different circumstances, it will be noted that opaque spots would result in a reduction of the reflecting power by a certain fraction which would be the same whatever the surrounding medium. This means that the ratio R(liquid)/R(air) would be constant. In other words, if points are plotted with R(liquid) as ordinates and R(air) as abscissæ they should all fall on straight lines passing through the origin. This, in general, has not been found to be the case.

The effect of a surface layer might be accounted for by introducing its hypothetical refractive index m' and calculating what this would have to be to give the observed diminished reflecting power. When such a calculation is extended to cover the case of an added

overlying medium the curves of R(liquid) and R(air) are found to be lines curving with the convex side downwards. The results of the present investigation do not fit such curves any better than the straight lines mentioned above, so we may safely conclude that neither of these classes of defect was prominent in the surfaces used.

We may then study the results with the view of determining if

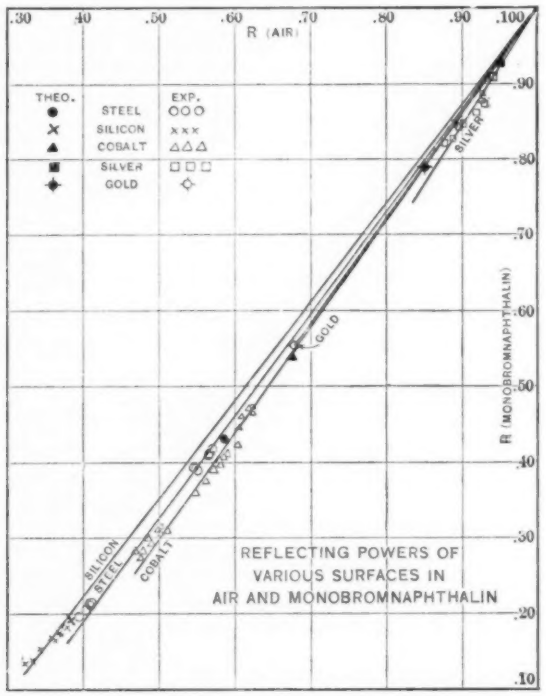

Fig. 2.

possible the effect of the more common class of defects, such as scratches and corrugations, on the optical properties here studied. Drude [1] found that sharp scratches had, in all cases save that of steel, a very decided effect in reducing the angles of principal incidence and hence the apparent refractive indices. But when these sharp scratches are removed by rouge polishing, although the metal may then give nearly its normal optical constants, its reflecting power may

[1] Wied. Ann., 39, p. 481, 1890.

still be considerably below the theoretical. Examination with a glass shows that the scratches have been merely rounded off into a myriad of minute corrugations with many small holes, and this, in the writers' experience, is the type of metal surface produced by the customary grinding and polishing process — buffing being excluded as it destroys the figure of the surface. In special metals, as already noted, these defects may be minimized so that a practically perfect surface results.

The results of a large number of observations on many different surfaces of this sort are given in the curves of Fig. 2. The abscissa of each point is the reflecting power of the corresponding surface in air, and the ordinate that in monobromnaphtalin — that liquid proving the most satisfactory to use. Points showing the lowest reflecting power correspond to surfaces having the most scratches or corrugations. Theoretical points for perfect surfaces, which are shown as small black circles, squares, etc., are derived from the optical constants of each metal tested.

Empirical Law.— It will be noted that for each metal the points for the different surfaces all fall fairly well on a straight line passing through the point (1, 1) and therefore having the equation $[1 - R(\text{liquid})]/[1 - R(\text{air})] = \text{a constant}$. Moreover, the lines for the different metals have very nearly the same slope. The small deviations of points from these lines are readily explained by the presence, in small measure, of defects of the first two classes above discussed, which could not be entirely eliminated. Not only do the points for surfaces of various qualities fall on these lines, but also those for theoretically perfect surfaces, as well as for the nearly perfect surfaces actually studied.

This then, the writers believe, is the law which expresses the relation between reflecting powers in air and in some other medium for metal surfaces of all degrees of polish, presupposing that surface layers — for example oil films — and spots such as oxidation and dirt are guarded against.

The theoretical basis of the law is not apparent. The action of scratches and corrugations on the incident light is undoubtedly twofold,— viz., to introduce in some cases more than one reflection and hence greater absorption; and to scatter in various directions a

fraction of the incident light. As the present method of investigation utilized a conical beam of small solid angle, rather than strictly parallel light, it is possible that the poorer sort of surfaces might show a somewhat higher reflecting power than if measured by a method using only parallel light; for in the present case some of scattered light might still fall within the limits of the cone which reaches the measuring instrument. However, as reflecting power under these circumstances in somewhat a matter of definition, neither method has an obvious advantage.

These considerations enable us to suggest a possible explanation of one result of experiment. It will be noted in the case of the poorer sort of surfaces of any one metal, that the fractional reduction of reflecting power on overlaying with monobromnaphtalin is much greater than for the better surfaces. We may suppose that for such a surface the portion of the incident light reflected is scattered into a cone of solid angle ω', of which only ω can reach the instrument. When covered with liquid the fraction reflected — less, of course, than if the liquid were not present — is scattered into the same cone ω' which on emerging from the plane surface of the liquid becomes, following the ordinary laws of refraction, a cone of wider angle ω''.

Consequently a still smaller fraction of the returned light reaches the spectrophotometer than in the first case and this would account for the observed result. But this does not by any means explain the fairly exact relations which experiment shows to exist and which cannot reasonably be ascribed to any particular instrumental arrangement.

Cathode Surfaces. — The few cathode surfaces of iron and platinum which were tested were deposited with a rather high current density, and while they showed perfect mirror surfaces, their reflecting powers were considerably less than the normal for these metals. When experimented on with various liquids their results did not agree with those for polished surfaces, but the discrepancy was greatly reduced when the actual optical constants for these surfaces were measured and introduced into the formula. When plotted as in Fig. 2 the points for these surfaces fell on lines somewhat intermediate between those on the diagram and one through the origin. This might mean the presence of metal in a finely divided state,

e. g., platinum black, and some color is lent to this view by finding that the reflecting power of these surfaces could be improved by polishing with rouge and chamois.

However, as noted by all who have worked with cathode surfaces, including Skinner and Tool,[1] and one of the writers,[2] they may be produced in a variety of forms according to the conditions of deposit, varying from a state resembling that of the fused metal to states widely different from this. Accordingly, without special and more or less exhaustive study of these optical properties for this kind of surface, it is impossible to draw definite conclusions. But it may be noted in this connection that one of the writers,[3] in studying the effect on the magnetic rotation (Kerr effect) produced by overlaying iron surfaces with various liquids, found that cathode surfaces obey the theoretical law (rotation proportional to the index of the liquid) better than polished surfaces.

Summary.

1. The extension of the formula for the reflecting power of a metal in terms of its optical constants, to include the case where the metal is covered by a transparent substance of any optical density, is experimentally justified for the case of perfect or practically perfect surfaces. This extension is made by replacing in the formula the actual refractive index n of the metal by the relative index n/m, where m is the index of the covering medium, the absorption index k of the metal remaining unchanged.

2. When a surface has a reflecting power lower than its normal value for that metal this condition is due in most cases to the presence of minute scratches, corrugations or indentations. While it is difficult to treat this case theoretically, the experimental results indicate that for all this class of surfaces as well as for those theoretically perfect, the relation $[1 - R(\text{liquid})]/[1 - R(\text{air})] = \text{a constant}$, exists for any particular metal.

Physical Laboratory,
University of Wisconsin,
June 8, 1909.

[1] C. A. Skinner and A. G. Tool, Phil. Mag., December, 1908.
[2] L. R. Ingersoll, Phil. Mag., July, 1909.
[3] Ibid.

ON THE PHOTO-ELECTRIC EFFECT WITH THE ALKALI METALS. II.[1]

The Dependence of the Photo-Electric Current on Light Intensity.

By F. K. Richtmyer.

IN a previous article[1] the writer has shown that the photo-electric current from a Na surface under the action of light from an incandescent lamp is proportional to the intensity of the incident light from very low intensities up to intensities in the neighborhood

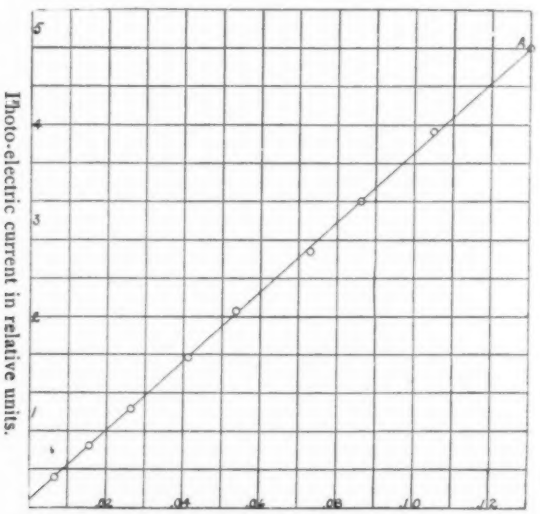

Fig. 1.

of .5 candle-foot. For purposes of comparison a portion of the curve previously shown is reproduced here (Fig. 1), the point marked *A* corresponding to an intensity of illumination of about .15

[1] The first paper in this series was published in The Physical Review, Vol. XXIX., 1909, pp. 71–80, under the title "The Dependence of the Photo-electric Current on Light Intensity."

candle-foot. The exact intensity was not measured partly because the nature of the experiment would not permit, partly because a knowledge of the exact intensity would have no value, the photo-electric current depending quite as much on the quality of the light as on its intensity.

In view of the fact that some observers had found that this linear relation did not exist if very great ranges of intensities were used, it seemed wise to extend the above investigation to the highest obtainable light intensities consistent with accuracy. It seems quite reasonable to expect that an intensity of illumination might be reached at which a phenomenon akin to saturation might be observed.

The apparatus, a modification of that described in the previous paper, is shown in Fig. 2. The positive terminal of a 12-volt

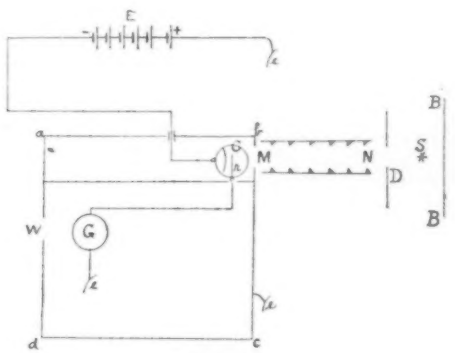

Fig. 2.

battery E is earthed. The negative terminal is connected to the sensitive surface (Na) of the photo-electric cell C. The platinum receiving wire r is connected to earth through the sensitive D'Arsonval galvanometer G, whose constant is $156 \cdot 10^{-11}$ amp./mm. at a scale distance of 138 cm. The cell and galvanometer were enclosed in a black box *abcd*, with windows at W and M, MN being used as before described to protect the cell from the light of the room. The source of light was a hand-feed, direct-current arc, S, of solid carbons placed at right angles to each other. A water cell (not shown) was placed at M to prevent a rise in temperature of the cell due to radiation from the arc. Behind the arc was a

black screen *BB* and a second screen at *D* was placed so as to prevent the light from striking the walls of the box *MN* and yet not cast a shadow on the cell. The variation in intensity of illumination was obtained by varying the distance *MS* of the arc from the cell.

The difficulties noted in the previous paper, *i. e.*, the currents due to contact E.M.F. and the fact that the walls of the cell are slightly conducting, were far too small to be of any disturbance in comparison with the currents obtained in this experiment. But great difficulty was experienced in handling the arc. The well-known fluctuations not only in the intensity but in the quality of light from the arc, even though the arc length did not vary greatly, caused variations in the photo-electric current of from 20 per cent. to 150 per cent. After much time had been wasted in trying to get readings under these conditions it was noted that, for ten or fifteen seconds after lighting the arc, the galvanometer reading would not vary considerably, possibly not more than two or three per cent. And, further, if the arc was put out and then immediately relighted before the carbons had time to cool very much, the galvanometer would come back to the same place as before. It was also found that this condition was very much improved by increasing the arc length to just beyond the hissing point and running the current up somewhat above normal. Although rather difficult to work with, a constant and fairly intense light source was thus at hand.

The procedure in taking observations was then as follows: The arc was first lighted and allowed to burn until the carbons became thoroughly heated. It was then "blown out," relighted by bringing the carbons together, and the vertical carbon run down, increasing the arc length until the hissing stage was just past. The spot of light on the galvanometer scale was watched for the next few seconds and its mean position recorded. This process was repeated until several readings were obtained for each intensity of illumination used. Not all of these attempts resulted in a reading, for sometimes, after relighting, the arc would never get quiet. It would, however, generally settle down again on a second trial.

The data thus obtained are shown in Table I., and graphically in Fig. 3, the candle power of the arc being approximately 1,900 as measured by a Weber photometer.

TABLE I.

Distance of Arc from Cell.	Galvanometer Readings.				Average Galvanometer Deflection.	Photo-electric Current. Amp. $\times 10^9$.	Illumination on Cell. Candle-feet.
10.00 ft.	3.8 mm.	3.7 mm.	3.8 mm.		3.8 mm.	5.9	19.0
8.00	5.5	5.8	5.8		5.6	8.7	30.0
6.50	8.0	8.0	8.0		8.0	12.5	45.0
5.50	10.0	10.5	11.0		10.5	16.4	63.0
4.75	15.0	15.0	14.0	14.0 mm.	14.5	22.6	84.0
4.00	21.0	19.5	20.0	20.0	20.1	31.4	118.0
3.50	26.0	24.5	23.0	26.0	24.6	38.8	155.0
3.00	32.0	34.0	34.0	35.0	33.7	52.6	210.0
2.50	51.0	50.0	52.0		51.0	79.5	304.0
2.25	63.0	61.0	63.0	63.0	62.5	97.5	375.0
2.00	79.0	78.0	80.0		79.0	123.0	475.0
1.75	100.0	107.0	95.0	105.0	103.0	160.0	620.0

Fig. 3 seems to show pretty clearly the linear relation between the photo-electric current and the intensity of illumination, even for

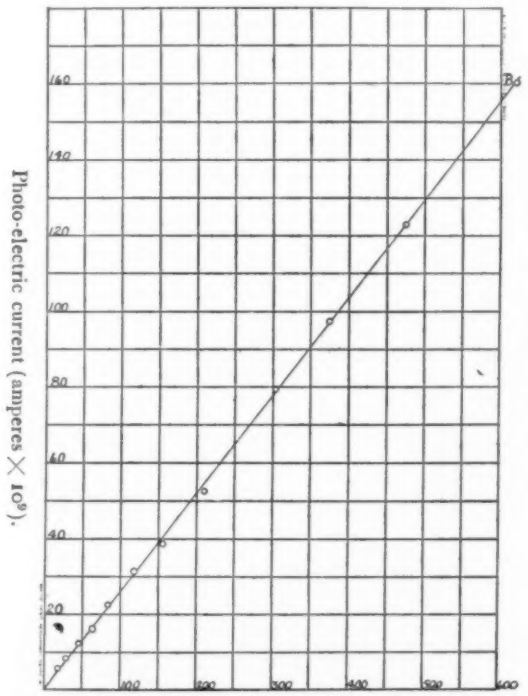

Fig. 3.

the extremely high intensities used here. The difficulty in controlling the light source accounts for the observations not giving quite so uniform a line as in Fig. 1, where an incandescent lamp was used. But even up to the highest intensities there is not the slightest suggestion of saturation.

These two curves present an interesting case not only of the extremely wide range over which a physical law holds, but also of the accuracy with which observations may be made at both extremes of the phenomenon, a fact more clearly brought out when the relative scales of the two curves are taken into account: If Fig. 3 were plotted to the same scale as Fig. 1 it would make a line 1,700 feet long!